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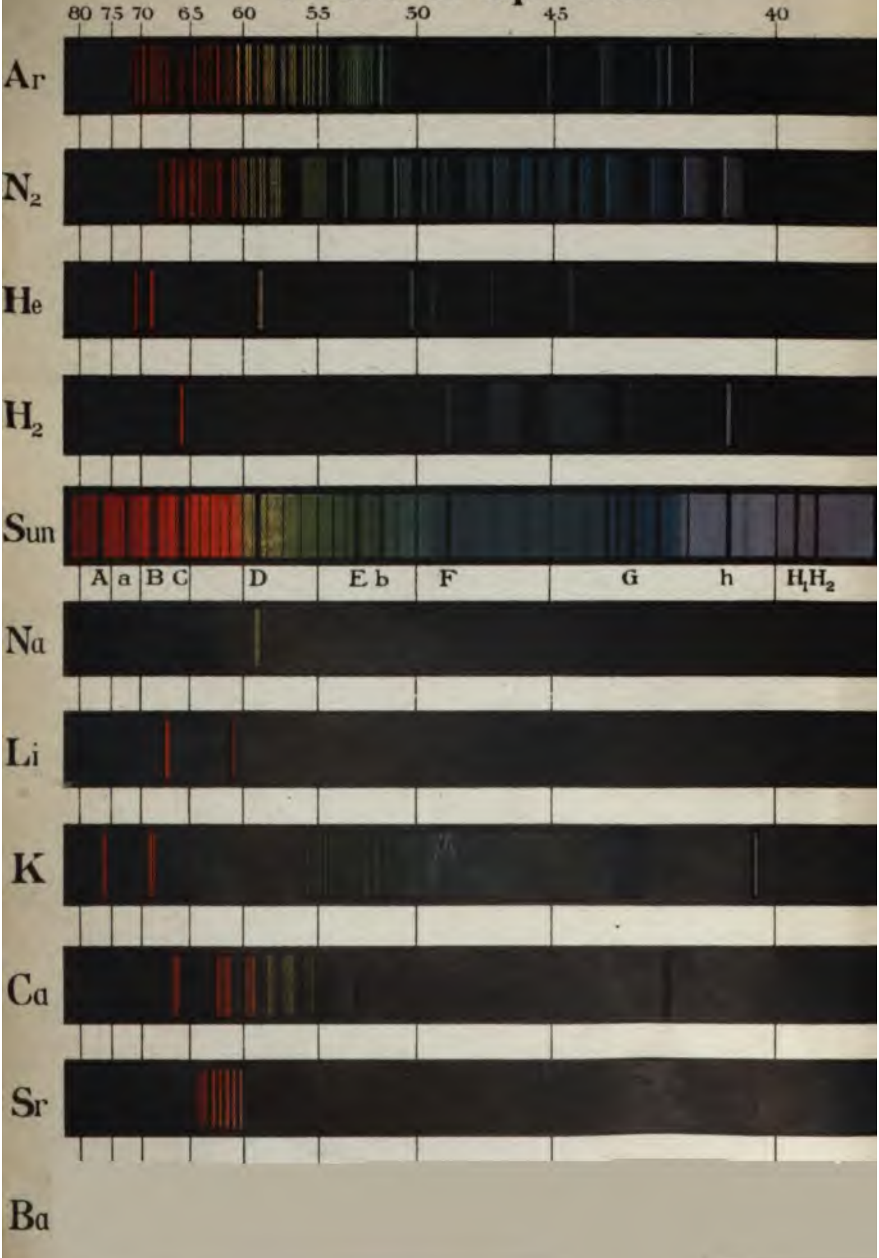

GENERAL CHEMISTRY

BY

HAMILTON P. CADY, Ph. D.

PROFESSOR OF CHEMISTRY IN THE UNIVERSITY OF KANSAS
AUTHOR OF "INORGANIC CHEMISTRY"

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PREFACE

This book is something of an abridgment and much of a simplification of the author's earlier book entitled "Inorganic Chemistry." It is intended for classes which have less time to devote to the subject than those for whom the former book was prepared. In it the author has preserved the general arrangement and spirit of the "Inorganic Chemistry," and has avoided a long more or less theoretical introduction, developing the subject as logically as possible from the descriptive and experimental side; each law and theory has been presented at the point which seems best fitted both to the student and to the subject.

Perhaps the most marked difference from the former book is to be found in the treatment of the atomic theory. The author feels that the recent advancements have justified a more unqualified support of this theory than was accorded it in the former work. By introducing an experimental conception of molar weights before taking up the chapter on atomic weights, the author feels that he has been able to develop the conception of atomic weights in a very simple manner from the experimental standpoint. The theory is then brought in as an explanation for the facts previously discussed.

In the preparation of the present book, the author has gladly availed himself of all the suggestions which have come to him from others who have had experience with his former book. He feels very grateful to Dr. Paul V. Faragher for advice in some difficult places, and especially so to his wife, Stella G. Cady, for loyal assistance in preparing the manuscript and reading the proof.

HAMILTON P. CADY.

LAWRENCE, KANSAS,
September, 1916.

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GENERAL CHEMISTRY

CHAPTER I

INTRODUCTION

Chemistry is a branch of natural science and deals principally with the properties of substances, the changes which they undergo, and the natural laws which describe these changes.

It is a very difficult matter to convey thought from one person to another by means of words, and anything like accuracy can only be attained when the words have as nearly as possible the same meaning to each. For this reason it is necessary to discuss at some length the significance, in connection with chemistry, of some of the terms used in the opening statement.

Properties of Substances.—We are able to perceive objects around us. Each of these objects is called a body and the signs by which it makes its presence known to us are called the properties of the body. When we find ourselves surrounded by a number of different bodies we instinctively begin to arrange them into groups according to certain points of similarity in their properties. We may for example form a class of bodies called bottles and group together all objects having the general shape of bottles. When we come to examine the different members of the class, we find that they possess marked differences in properties, other than those of shape or size. Accordingly, we at once set up a number of sub-classes such as glass bottles, stoneware bottles, rubber bottles, etc., and say that these differ because they are made of different substances. Substances then, are the things of which bodies are made. As examples of substances we may give iron, salt, sugar, lead, etc.

It now remains to distinguish between the properties of bodies and those of substances. This distinction may be brought out by considering what we do in forming the sub-class glass bottles.

In grouping the glass bottles together, we pay slight attention to the properties of shape and size, but look to other characteristics which we say are the properties of the substance glass. Every part of a glass bottle presents the properties of the substance glass, and to precisely the same degree as every other part; further, if the bottle be broken into pieces, that body will cease to exist and in its place there will be a collection of bodies called
pieces of glass. If w and size, the properties of
all these bodies are ical with those of the glass
bottle from which the The properties of bodies,
then, aside from those ize are the properties of the
substance from which e made. The properties of
the body, as such, are pe and size. A given body
cannot be a barrel unle ain shape and is of a definite
size; if it is larger it is smaller, a keg.

Changes.—Experience that the properties of substances can be altered in various ways.

Every alteration constitutes a change, and for purposes of convenience, changes are arbitrarily divided into two classes, physical and chemical.

A physical change is one which alters only a very few of the properties of a substance. The moving about of a body or the heating of a piece of iron are examples of physical changes.

A chemical change is one which alters all or nearly all of the properties of a substance. In fact, after a substance has undergone a chemical change, we are unable to recognize the presence of the original substance, and in its place we find one or more new substances with different properties. The burning of wood or the rusting of iron are familiar examples of chemical changes.

From these definitions it would seem to be an easy matter to decide whether a given change is physical or chemical. And so it is in most cases. However, there are all gradations in the number of properties altered in the change, and in some cases it becomes really impossible to decide definitely to which class they belong. This is due to the fact that there is no real difference between the two changes; we have simply arbitrari drawn a distinction as a matter of convenience in our gener scheme of classification. The freezing of water is an example of a change which it is difficult to classify. So many of the operties of ice are different from those of water that one is clined to call freezing a chemical change, but on the other hand he transformation takes place so easily, simply upon changing he temperature, that probably the majority of people consider t a physical change.

In most cases there is no difficulty. For example, a piece of rubber when rubbed with woolen acquires the property of attracting bits of paper, but is not otherwise altered. Without question this is a physical change. If the rubber be brought in contact with a flame, it will take fire and burn with a smoky flame and continue to do so until all the rubber has disappeared. Soon after the rubber begins to burn a very strong odor will be noticed which must be due to something produced from the rubber. Since we have in this case the complete disappearance of the properties of rubber and the appearance of the properties of a new substance, this is a chemical change.

Natural Laws.—Having discussed the properties of substances and the changes which they undergo, we may now turn to the natural laws which describe these changes.

Experience tells us that under like conditions events repeat themselves in a very large measure, and that the more nearly the conditions are reproduced the more closely are the events duplicated. So generally is this the result of our experience that we finally become convinced that if it were possible to reproduce the conditions exactly, the events would be exactly duplicated. As a result then of our experience we are able to say, after repeated trials, just what takes place under certain conditions. Such a statement is a law of nature. A law of nature differs then essentially from a law of man in that it is simply a statement of what does happen and has in it no element of compulsion. Man is so insignificant a part of nature that he cannot presume to dictate to her but can only observe, and learn to make the condition such that the operations of nature shall be as favorable to himself as possible. A law of nature is a statement of the way nature works and should be so worded that it describes as large a number as possible of single phenomena and gives us the maximum amount of information concerning each.

As an illustration of a law of nature, we may select the law of falling bodies. We know as a matter of common experience that heavy bodies if unsupported fall to the earth, and a statement to this effect is a law of nature. It would be much more useful if it gave us the results of our experience as to the velocity of the bodies after falling for given times and in addition the space passed over during certain times of fall. The law might then be worded as follows: "All heavy bodies fall toward the earth with a velocity which is equal to the force of gravity times the time that the body has been falling and the space passed over is equal to one-half the force of gravity times the square of the time of fall."

Obviously from what has been said the wider our knowledge of the laws of nature the better equipped we are for life. They are all directly or indirectly the results of experience and their formulation is one of the most important works of science.

The Fundamental Law of Chemistry.—We find upon examining the properties of different bodies composed of the same substance that they agree exactly in all their essential properties, that is, the properties other than those of shape and size. We find too that other substances have radically different properties and that the change from one to another is sudden, leaving gaps which are not filled in by gradual alterations in the properties. We have then as many absolutely distinct sets of unvarying properties as there are substances.

Bodies may be arranged in classes such that the different members of each class agree exactly with each other in all their essential properties. The different members of each class are the bodies composed of the same substance. The law just given is known as the law of the definiteness of properties and is often called the fundamental law of chemistry.

Properties of a Substance and the Substance.—We have defined properties as the signs through which objects manifest themselves to us and have spoken of them as though they belonged to substances, and of the substances as though they in some way possessed the properties. Indeed the original meanings of the words would convey these ideas, and it is very hard to get away from them. However, when we come to consider just what there is about a substance which is not a property of that substance and which might be that which possesses the properties we are completely at a loss. Everything that we know about a substance is a property of that substance and if by experimentation we find out anything more, that will also be a property; farther than this it seems to be impossible for us to conceive of anything concerning a substance that is not a property of that substance. One can be readily convinced of this by trying to think of anything about a familiar substance that is not a property of that substance. A realization of this fact does not make our conceptions of the substance any the less definite because these properties are the real things about the substance, which we can know and measure. In fact our idea of the substance is simply the sum of all these properties which we know. For us then a substance is simply *a specific group of essential properties which always occur together and to an unvarying degree under given conditions.* This may be used as a working definition of a substance. If there is anything more to a substance than its properties we can know nothing of it. We cannot even imagine anything about it. So we will leave the question of the actual existence of a possessor of properties to speculative philosophy, and in matter of fact chemistry when we say substance we will mean properties.

Every known substance has a name which in a way stands for the properties of the substance. These names can mean to us only as much as we know of the properties of the substances. So in studying chemistry we must take care that we do not merely learn the names of the various substances with which we deal, but also that we make these names mean something to us by learning the more important properties of the substances.

Physical and Chemical Properties.—It is convenient to divide properties into two classes—physical and chemical. A physical property is one which can be detected and measured without causing the substance to undergo more than a physical change. As examples we might give color, density, conductivity for heat or electricity, etc.

A chemical property is one which is only revealed when the substance is transformed into something else and consequently undergoes a chemical change. One of the properties of sulfur is that it burns with a pale blue flame, and finally all disappears, leaving behind something which is invisible but which has a very strong smell. Since this property is shown only when the sulfur is transformed into a new substance, this is, therefore, a chemical property.

Since there is no real difference between physical and chemical changes, there is none between the two sets of properties, but nevertheless, it is convenient to make the arbitrary distinction.

Identification of S chemist is very often confronted with the prob as to whether two different bodies are composed of f different substances. The decision rests upon the a he question, Do the bodies have exactly the same ess rties? If they do, they are composed of the same f they do not, of different substances. Evidently can only be answered after carefully investigating s. To be perfectly sure, it would seem to be necessary npare all of the properties because two substances might agree in most of their properties and yet differ enough in some to make them different substances. The labor required for the comparison of all of the essential properties is so great that it is never done. The chemist compares some of the essential properties, and if these agree exactly he decides that the two bodies are composed of the same substance. In doing this he takes advantage of a law which states that if two bodies agree exactly in some few of their essential properties they will agree exactly in all and are composed of the same substance.

The Characterization of a Substance.—The properties chosen for investigation in order to characterize a substance vary with the case, but naturally they are, in general, those which can be most readily observed and measured, or else they are the ones in which the substance differs most from other substances.

The impressions produced upon our sense of sight, taste, and smell can be very easily determined, and are but rarely omitted. The physical state (solid, liquid, or gaseous) of the substance at ordinary temperature and pressure and the conditions under which it changes from one state to another are easily determined and important properties. The solubility of a substance in water is another valuable characteristic. A few words concerning some of these frequently studied properties would seem to be in order here.

Physical States.—We distinguish three different ways in which substances fill space and call these the physical states, giving them the names solid, liquid, and gaseous states.

The Solid State.—A substance is a solid if a given body composed of this substance has both a definite volume and a definite shape of its own independent of its surroundings.

The Liquid State.—A substance is a liquid if a given body composed of this substance has a definite volume but takes its shape from its surroundings. A liquid always runs down to the lower part of the vessel in which it is placed and takes on the shape of the vessel in so far as it can fill the container. The free surface of a liquid tends to be flat and parallel to the surface of the earth unless the body of the liquid is small, when the surface is rounded. If the body of liquid be very small and the surface entirely free, the liquid takes on the form of a sphere modified more or less by the action of gravity.

The Gaseous State.—The gaseous state is characterized by the fact that a gaseous substance has neither definite volume nor shape, but always fills the container in which it is placed and consequently takes its shape and volume from the surroundings.

It is a very easy matter to tell, in the great majority of cases, whether a given substance is solid or gaseous. There are, however, a few substances which are like wax in that they keep a fairly definite shape for some time and so give the impression that they are solids. If left for a longer time they slowly change their shape and flow, thus showing that they are really viscous liquids. But such substances are comparatively rare and give but little trouble in classification.

The physical state of a substance may vary with the conditions such as temperature, etc. With rising temperature, solids always tend to become either liquid or gaseous, and liquids to become gaseous. With falling temperatures gaseous substances always tend to become either liquids or solids, and liquids to become solids.

Solubility and Solution.—Many substances when brought in contact with water mix with the latter in varying proportions and form a homogeneous liquid which has in a general way the properties of the water and of the other substance. Such a homogeneous mixture, *i.e.*, one in which every distinguishable particle is exactly like every other particle in essential properties, is called a solution. The ability of a substance to form a solution is called its solubility and is an important property of the substance. A more extended discussion of solution will be given at a later point, where it will be shown among other things that solutions are not necessarily liquid but may be solid or gaseous as well.

Mechanical Mixtu s are often present together in such a way that t a homogeneous mixture but the different parts n hed and more or less easily separated. Such n lled mechanical mixtures. Muddy water may b example of such a mixture. Examine it with a l rticles of silt can be seen. Allow it to stand or p a filter and the silt may be separated from the w water is not homogeneous and hence is not a solution. Solutions stand between mechanical mixtures and a very important class of substances, with which we will become familiar in a little time, known as chemical compounds.

CHAPTER II

UNITS

Units.—Some of the properties of substances, as for example color, can be ascertained by simple inspection, while others require more or less elaborate experiments to bring them to light. The constant aim is to represent these properties by numbers. To do this a unit must be decided upon and the property carefully measured in terms of this unit. Almost all of the units used in scientific work are derived directly or indirectly from three fundamental units, the centimeter, the gram, and the second, and the whole scheme of units is called the C. G. S. system. The second is the unit of time. It is in use in daily life and is familiar to everyone.

Length.—The centimeter is the unit of length and is the one-hundredth part of the length of a certain bar of platinum carefully preserved in Paris, which is called the "Standard Meter." This standard meter was intended to be the $^1/_{10.000.000}$ of the earth's quadrant or quarter circumference, measured on the meridian of Paris, but afterward turned out to be something different from this owing to an error in the measurement. An inch is equal to a little more than 2.5 cm.

Mass.—The gram is the unit of mass. It is the $^1/_{1.000}$ part of the mass of a certain piece of platinum called the standard kilogram. It was intended that the gram should be the mass of a cubic centimeter of water at its temperature of maximum density, 4°C., but actually the mass of the latter is 0.999982 grm. This differs so slightly from unity that the mass of 1 c.c. of water at 4°C. is usually taken as exactly 1 grm.

Weight.—A heavy body is always pulled toward the earth with a certain force. This force is called its weight and is proportional to the mass of the body. The weight of a given body varies with its position on the earth, but an average is 981 dynes for each gram of the body's mass. A dyne is that force which acting on 1 gram for 1 second will generate a velocity of 1 cm. per second.

If one takes as the unit of weight, not the dyne, but, as is commonly done the weight of 1 grm., then the numerical value of the weight of a body in terms of this unit is the same as the mass of that body. The statement that a body has a weight of 10 grm. means that its weight is the same as that of 10 grm., 9,810 dynes say, and consequently the mass is 10 grm.

Volume.—The unit of volume is the cubic centimeter or the still larger unit, the liter which is 1,000 c.c.

Energy.—Work is usually defined as the product of a force and the distance through which it acts: energy as work or the ability to do work. It has been further shown that there are many forms of energy such as heat, light, electrical energy, chemical energy, etc., and that these forms may be changed one into another without loss. In fact *in an isolated system of bodies, energy can be neither created nor destroyed, but remains present in unchanged amount.* This is the law of the conservation of energy.

The unit of energy is the erg, and this is the work done by a force of 1 dyne acting through a distance of 1 cm. This unit is rather small, and so we have the larger units, the joule, which is 10,000,000 ergs, and the kilojoule which is 1,000 joules.

Whenever work is done upon a body, the latter acquires the ability to do work, and hence an increase in energy. The simplest way to regard this change of work into energy is to consider work as one of the forms of energy. If this is done *energy may be defined as work and everything else which may be obtained from work and reconverted into work.*

Conservation of Weight and of Mass.—One of the most useful instruments to the chemist is the balance. This is a device by means of which the weights of bodies may be compared, and since the weights are proportional to the mass, the relative masses may be determined.

If we ask the question, how are the masses of substances affected when they undergo chemical change, we can obtain the answer by weighing the reacting substances before and after the change. We will find that in many cases there are apparent losses in weight, as in the case of burning a piece of wood and in other cases a gain in weight, as in the rusting of iron. But these changes take place in contact with air and hence the changes in weight may be due to something escaping to the air in the case of the wood, or coming in from the air in the case of the iron.

This possible source of change in weight may be excluded by sealing the whole reacting substance air-tight in a flask. When this is done, it will be found that whatever changes in weight may be observed will be inside the limits of experimental error, for all but the most refined experiments, and even in these cases the small changes observed may perhaps be due to some source of error as yet unknown.

Neither is there any known physical change which will alter the weight at any given spot of the substance undergoing the transformation and therefore we at once set up the law of the conservation of weight which is, that *neither a physical nor a chemical change alters the total weight of the system undergoing change.*

Since mass is proportional to weight we may get from the above the law of the conservation of mass. *The total mass of a system is the same before and after any chemical or physical change which may take place within the system.* This simply means that although chemical changes alter so radically the other properties of substances they do not change that property called mass.

Density.—The density of a substance may be defined as the ratio of the mass of a given body composed of that substance to the volume of the body. It is expressed in terms of grams per cubic centimeter.

Specific Gravity.—The specific gravity of a substance is the ratio of the weights of equal volumes of that substance and of some other substance taken as a standard. Water is usually taken as the standard. The temperature of both substances must be stated in order that specific gravity may be definite. If water at 4°C. is taken as the standard substance, since at that temperature its density is one, the numerical value of the specific gravity will be the same as that of the density, although the conceptions are entirely different.

CHAPTER III

OXYGEN

Discovery of Oxygen [illegible] discovered August 1, 1774, by the English chemi [illegible] o prepared it by heating mercuric oxide. It wa [illegible] y discovered something like a year earlier than by [illegible] e Swedish chemist Scheele, but his results were n [illegible] til 1777. Scheele obtained it by heating saltpeter, mercuric oxide, manganese dioxide, and a number of other substances.

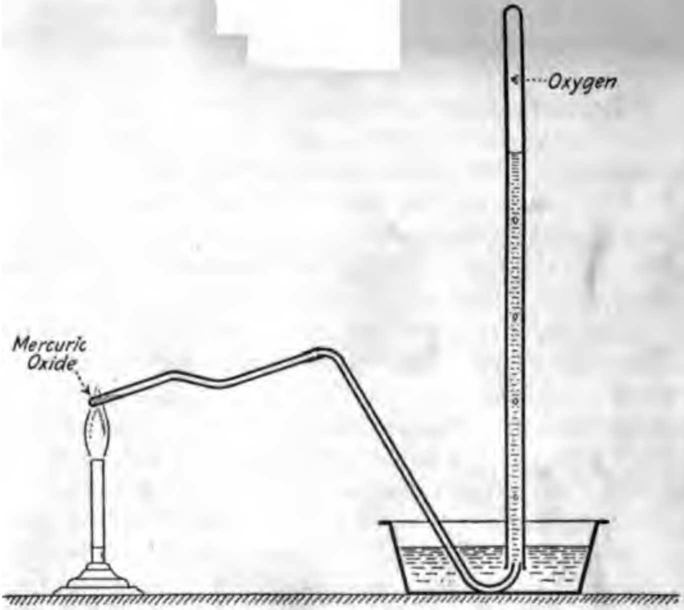

Fig. 1.

Priestly's original experiment, in a somewhat modified form, may be easily repeated. Mercuric oxide, which is a reddish powdery substance, is placed in a doubly bent tube (Fig. 1) which must be of hard glass. It is then strongly heated, and soon the mercuric oxide darkens in color and becomes almost black. If the heating be continued a bright metallic film appears on the cooler part of the tube, and at the same time, if the end of the delivery tube be placed under water, bubbles of gas will be seen to rise through the water. This gas may be collected by filling a vessel with water and placing it mouth downward in a trough of water. Upon bringing the mouth of the vessel over the delivery tube, the bubbles of gas will pass up into the vessel and gradually displace the water. When the vessel is full of the gas it may be removed from the water and placed mouth upward on the table for experimentation, taking care to keep it covered with a glass plate. It will be as transparent as air and in fact will appear just like air. It may, however, be distinguished from air by its action toward a feebly glowing spark on the end of a splinter. In oxygen the spark bursts into flame, while in air it barely continues to glow.

If the process of heating the mercuric oxide be continued, the oxide will be seen to diminish gradually in quantity and the bright metallic film to increase, and all the while the gas—oxygen—will be given off. This will go on until the mercuric oxide has all disappeared, then the process comes to an end. If the bright metallic film be examined it will be found to consist of drops of mercury, which is often called quicksilver. So we have the one substance, mercuric oxide, decomposing into two substances, oxygen and mercury which have entirely different properties from the mercuric oxide; therefore, this is a chemical change.

Combustion.—Experience from infancy has made us familiar with that most important set of chemical phenomena called combustion. We see the coal or wood burn in the stove, the oil or gas in the lamps. We know that a great amount of heat is universally given off during such a process. In most of the above-mentioned cases, it is very apparent that the burning substance decreases in weight. There are, however, other cases which we would certainly classify as combustion in which the weight is increased during the process of burning. For example, if a piece of metallic magnesium, in the form of a ribbon, be held in the flame of a match it will take fire and burn with an exceedingly bright light. The metal disappears and in its place is left a white powdery substance which weighs two-thirds more than the metal did before burning. Finely divided iron will burn when brought into a flame, forming a black brittle substance which weighs more than the original iron. In these and other instances of the same kind which might be mentioned, the products of combustion are solids, and hence easily obtained in a weighable form. This suggests that perhaps in every case of combustion the products are really heavier than the con ice, and that in the case of the wood, etc., first products are gaseous and hence escape our obs t this is so may be easily shown in the case of ling a cold object over the burning lamp when it mes covered with a film of liquid water. Since not accumulate if the lamp is not lighted, we con vater is one of the products of the combustion of tr p of lime water, on the end of a glass rod or a loop of wire, be brought over the flame of a lamp it will quickly become clouded. Now water vapor will not produce this cloud in the lime water nor will it appear unless the lamp is burning, and therefore we conclude that something besides water is formed during the burning of the oil. One of the characteristic properties of carbon dioxide is its ability to cloud lime water, and we then conclude that carbon dioxide as well as water is formed during the combustion of the oil. Processes by which the presence of certain substances may be detected are called tests or reactions, and the substances used, such as the lime water in this case, are called reagents. By applying these same tests to burning coal, wood or gas, it will be found that in these cases also, carbon dioxide and water vapor are formed. If the coal is anthracite, comparatively little water vapor and much carbon dioxide will be produced.

There is a solid white substance called caustic potash which has the power to take up both water vapor and carbon dioxide, and to hold them in such a form that they may be weighed.

If a glass cylinder loosely filled with this substance be placed over an unlighted candle and the whole counterpoised upon balance and the candle then lighted (Fig. 2), the caustic po will absorb the water vapor and carbon dioxide produced du the burning, and it will be very quickly seen that the weight the whole is increasing, although the candle is visibly becomi smaller. In some such a way as this it may be shown that the weight of the products of combustion is always greater than that of the combustible substance. Since in every case the products of combustion have different properties from the original substance, the changes that take place are chemical changes.

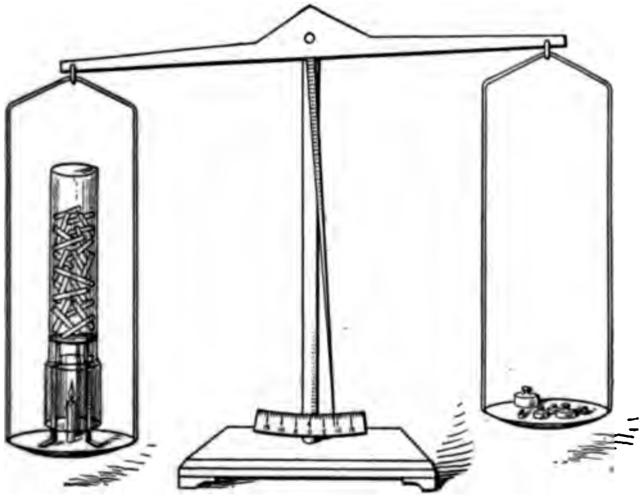

Fig. 2.

The law of the conservation of weight states that the weight of the products of a chemical change is the same as that of the substances before the change. We must conclude then that there is some other substance than that which burned taking part in the chemical change which we call combustion, and that the weight of this other substance is equal to the difference in weight between that of the products of combustion and the combustible substance.

Rôle of the Air.—All these changes which we have been considering take place in contact with the air, so it is very probable that this other substance is present in the air. This is confirmed by the fact that it is impossible to make a combustible substance burn in a vacuum, and further, when it burns in a limited amount of air a part of the air is used up, or disappears, but never more than one-fifth of the total volume of the air. After one kind of combustion has used up one-fifth of the air, no other substance will burn in the remaining four-fifths. This indicates clearly that the air consists of at least two gaseous substances, one present to the extent of one-fifth of the total volume; and taking a most important part in the phenomenon of combustion.

If mercury be heated for a number of days to a temperature a little below its boili tact with a limited volume of air, a reddish subs ic oxide, is formed on the ury, and the air gradually eases in volume. If the uric oxide obtained in this be heated as described on 2, it yields mercury and en, and the volume of oxy- so produced is just equal to the decrease in the volume of the air. This oxygen has the power of supporting combustion to an extraordinary degree and in the burning, all the oxygen may be used up. The residual air will not support combustion, but if the oxygen obtained by decomposing the mercuric oxide be added to it, the air regains all its original properties.

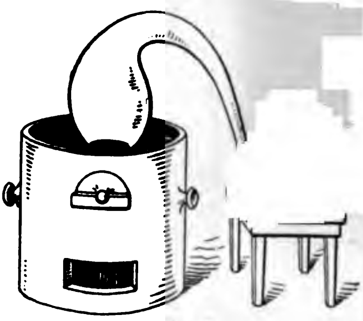

Fig. 3.

These experiments were first performed by the French chemist Lavoisier shortly after the discovery of oxygen, and had much to do with our present conception of combustion. The apparatus which he used is shown in Fig. 3.

Combination and Decomposition.—We have seen above that mercuric oxide may be transformed into mercury and oxygen. This process is an example of what is called decomposition, and the reversed process, the formation of the mercuric oxide from oxygen and mercury, is an example of combination. Processes like these compose a large part of the changes studied in chemistry.

Preparation of Oxygen.—Although free oxygen is present in the air in such enormous quantities, the problem of separatin from the substances with which it is mixed is by no means sim (See liquid air, pp. 25 and 200.)

There are many other substances besides those already giv which will yield oxygen upon being heated. Among these e mentioned potassium chlorate and potassium permanganate, nd in addition oxygen may be obtained by the decomposition f water by the electric current and by acting upon sodium peroxide with water or dilute acid. The method most in use in the laboratory is that of heating potassium chlorate. This is a white crystalline substance which melts at about 360°C. and decomposes at a higher temperature into oxygen and potassium chloride. The rate of decomposition increases rapidly as the temperature is raised. Curiously enough if it be mixed with something like one-third its weight of manganese dioxide the decomposition takes place much more rapidly than with the potassium chlorate alone, being quite active at as low a temperature as 200°C., and after the operation the manganese dioxide is found to be unaltered except, perhaps, that the particles may be a little finer than before. Although manganese dioxide will yield oxygen at a high temperature, it will not do so in noticeable quantity at 200°C., and its action here seems to be to greatly increase, by its mere presence, the rate at which the potassium chlorate decomposes. Actions of this kind are common and are known as catalytic actions. They will be considered more in detail later.

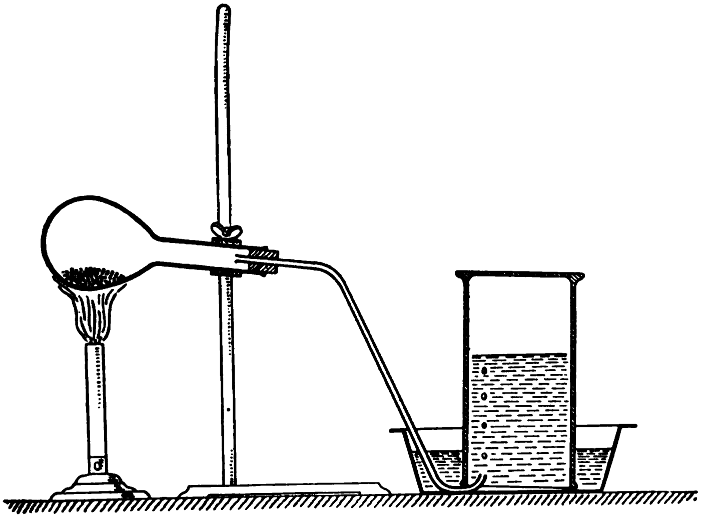

Fig. 4.

The decomposition of the potassium chlorate when mixed with manganese dioxide may be carried out in a hard glass flask (Fig. 4). The oxygen is collected by the displacement of water as explained above.

Physical Properties.—The gas so obtained is colorless, odorless, and not very soluble in water or it could not be collected over this liquid.

One of the important physical properties of every substance is its density. The simplest way to determine the density of oxygen is to decompose a known weight of either mercuric oxide or potassium chlorate and weigh the residue. The loss in weight is the weight of the oxygen. If the unit of weight is the weight of 1 grm. the loss in weight gives at once the mass of the oxygen; and to obtain its density it will only be necessary to measure the volume of the oxygen, and divide the mass by the volume. For example, 1.6000 grm. of mercuric oxide gave 0.1111 grm. of oxygen which measured 87.15 c.c. under a pressure of 74 cm. of mercury and at 25°C. The density of oxygen under these conditions is therefore $^{0.1111}/_{87.15} = 0.0012752$ grm. per c.c.

Standard Conditions.—If the volume of a gram of oxygen, or of any other gas for that matter, be determined under different atmospheric conditions it will be found to vary widely. Other things being the same, the higher the temperature, the greater the volume, and the higher the pressure the smaller the volume. It can be readily seen from this that the density of a gas is not definite unless the volume of a given mass of the gas be measured at a certain definite temperature and pressure. For the sake of uniformity it is the universal custom to take the temperature of melting ice, or 0°C., as the standard temperature since this can be so easily reproduced. As the standard pressure, is taken the mean pressure of the air at the sea level, which is equal to that of a column of mercury 76 cm. in height. Since the density of the mercury changes with the temperature, the mercury should also be at 0°C.

THE GAS LAWS

Boyle's.—As it is usually not convenient to measure the volume of gases under standard conditions, it is a matter of great importance to know just how they change their volumes with nges in pressure and temperature, so that their volumes may read under any convenient conditions and corrected to what ey would be under standard conditions. Fortunately it has en found that gases behave so nearly alike that the same corctions will do for all unless extreme accuracy is demanded.

The simplest relationship is that between the volume and the ressure, and this has been known ever since 1660, when it was iscovered by the English scientist Robert Boyle.

Boyle found that if the pressure upon a fixed mass of a given gas, at constant temperature, be doubled, trebled, or quadrupled, the volume of the gas would be reduced to one-half, one-third, or one-fourth of its original volume, or in other words *the volume of a fixed mass of a given gas at constant temperature is inversely proportional to the pressure.* This is known as Boyle's law, and may be represented as follows:

$$v = k\frac{1}{p} \qquad (1)$$

when v and p are the simultaneous values of the volume and pressure under which the gas is measured.

The above relation may also be expressed in the following form:

$$p_1v_1 = p_2v_2 = pv = \text{const.} \qquad (2)$$

where p_1v_1 and p_2v_2 are pairs of simultaneous values of pressure and volume. In words this is expressed as follows: *The product of the simultaneous values of the pressure and the volume for a fixed mass of a gas at constant temperature is a constant.* This is simply another way of wording Boyle's law.

As an example of the practical application of this law we may take the data given above for the density of oxygen. There we had 87.15 c.c. of oxygen at 25°C. and a pressure of 74 cm. of mercury. What would be the volume at the same temperature but under the standard pressure of 76 cm. of mercury?

Taking equation (2) we have

$$p_1v_1 = p_2v_2$$

and letting $p_2 = 74$, $v_2 = 87.15$ c.c. and $p_1 = 76$ cm. of mercury,

v_1 = volume at this standard pressure. Solving for v_1 we g

$$v_1 = \frac{p_2v_2}{p_1}$$

$$v_1 = \frac{74 \times 87.15}{76} = 84.85 \text{ c.c.}$$

This would be the volume of the gas if measured at the temper
ture 25°C. unde essure.

In order to c ne which the gas would occup
at the standard well as pressure, it would b
necessary to asc e of a given change in the tem
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volume of the ga pressure. As indicated abov
the volume of a increases with rising temper
ture, the pressure stant. If we take the volum
occupied by a certain mass of a gas at the melting-point of ice
0°C. as unity, and then heat the gas to the temperature of wat
boiling under a pressure of 76 cm. of mercury, the volume of th
gas will be found to be 1.367, so that the increase has been 0.36
If now we divide the difference in temperature between th
melting-point of ice and the boiling-point of water into 100 equ
parts, as has been done in the Centigrade thermometer syster
the increase in volume for each degree is 0.00367 or $\frac{1}{273}$ of th
volume at 0°C. This is called the coefficient of expansion of th
gas and is represented by alpha, "α."

The law describing this behavior is called **Gay Lussac's ar Dalton's Law** or sometimes **Charles' Law** and was discovere simultaneously by Gay Lussac and Dalton in 1802. It may expressed as follows: *The volume of a fixed mass of a gas at co stant pressure is increased by $\frac{1}{273}$ of its volume at 0° Centigra for each degree's rise in temperature.*

The mathematical expression is

$$v_t = (1 + \alpha t)v_o$$

where v_0 = volume at 0°C., v_t = the volume at the temperatu t, t = the temperature, and α the coefficient of expansio 0.00367 or $\frac{1}{273}$. The conditions under which this will ho are that both the mass of the gas and the pressure upon must remain constant.

lute Temperature.—Since all gases are so regular in their r toward changes of temperature the change in the of a fixed mass of a gas under constant pressure has ken as the measure of the change in temperature. Gas meters are really the standard instruments for the ement of temperature at the present time. ry thermometers are used as working instru- because they are somewhat more convenient as thermometers.

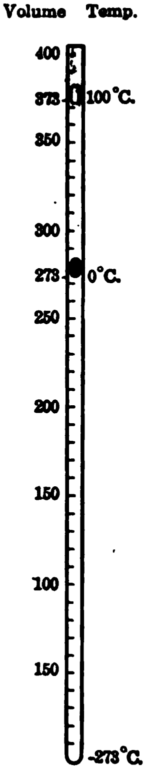

Fig. 5.

the Centigrade thermometer system, the g-point of ice has been called 0° and the -point of water 100°. If a fixed mass of a constant pressure be raised in temperature he melting-point of ice to the boiling-point er (Fig. 5), its volume will be increased by of its volume at 0°C. Since we have y decided to call the temperature interval n the freezing- and the boiling-point of 100° and to take the change in the volume as as the measure of the change in the tem- re, we say that if a fixed mass of a gas at nt pressure changes its volume by $\frac{1}{273}$ of ume at 0°C. its temperature has been changed . If it changes its volume by $\frac{20}{273}$ of its e at 0°C. the change has been 20°.

a very simple matter to cool a gas to a tem- re below 0°C. The gas contracts during the s and continues to do so as it is cooled to nd lower temperatures. In accordance with as been said above, we consider that the gas en cooled 1° for each $\frac{1}{273}$ of its volume at hich it has lost, the pressure and the mass of gas being nt. It is very obvious that a gas cannot lose more than of its volume because this would reduce it to zero . Therefore, the lowest temperature to which a gas cooled is 273 Centigrade degrees below the Centigrade d this temperature is called absolute zero. As a matter t all gases are liquefied or solidified before they reach mperature, and since the gas laws do not describe the behavior of liquids or solids the substances would doubtless have some volume even if cooled to absolute zero. The lowest temperature yet reached is about 3° above absolute zero which is the temperature at which liquid helium will boil under diminished pressure.

Temperatures reckoned upward from this absolute zero are called absolute tem he absolute temperature of melting ice is 273°A.. ng water 373°A. Temperatures on the Centigr y be readily changed to the absolute scale by adc he Centigrade temperature. Absolute temperatures a represented by T and Centigrade by t, so,

$$273$$

There are two import ges of the absolute over the Centigrade system. First, use one does away with all negative temperatures and second, we are enabled to state the law of Gay Lussac and Dalton in the following exceedingly simple manner. *The volume of a fixed mass of a gas at constant pressure is directly proportional to the absolute temperature.* In symbols this law is expressed as follows:

$$v = k'T \qquad (3)$$

where v is the volume, k′ the proportionality factor, and T the absolute temperature.

By a simple transformation of equation (3) we get

$$\frac{V}{T} = k'$$

or the volume of a fixed mass of a given gas divided by the absolute temperature at which it is measured is equal to a constant. From this it follows that

$$\frac{V_0}{T_0} = \frac{V_1}{T_1} \qquad (4)$$

in which V_0, T_0 and V_1, T_1, are any different sets of simultaneo values of the volume and temperature for the same sample gas.

With the aid of equation (4), we may readily calculate volume of a given sample of gas at one temperature from volume at another provided the pressure remains constant. This may be illustrated by calculating the volume of the oxygen obtained on p. 18 at the standard temperature of 0°C. or 273°A. On p. 20 we made the correction for pressure according to Boyles' law and found that at 25°C. or 298°A. and under the standard pressure, the volume would be 84.85 c.c. Letting V_0 be the volume at 273°A., V_1 be 84.85 and T_1 be 298°A., we get

$$\frac{V_0}{273} = \frac{84.85}{298}$$

or

$$V_0 = 84.85 \times \frac{273}{298} = 77.74 \text{ c.c.}$$

To obtain the density of oxygen under standard conditions all that remains to be done is to divide the mass of the oxygen, 0.1111 grm. by this calculated volume, 77.74 c.c.

$$\text{Density} = \frac{0.1111}{77.74} = 0.0014293 \text{ grm. per c.c.}$$

The Combined Gas Laws.—In calculating the volume of the oxygen obtained on p. 18 we first corrected for pressure by multiplying the measured volume 87.15 c.c. by the ratio of the measured pressure 74 cm. to the standard pressure 76 cm. and then took this result, 84.85 c.c., and corrected for temperature by multiplying it by the ratio of the standard temperature, 273°A. to that at which the gas was measured 25°C. or 298°A. Obviously these operations might just as well have been combined and the double correction made at once, as follows:

$$V_0 = 87.15 \times \frac{74}{76} \times \frac{273}{298} = 77.74 \text{ c.c. at } 0°\text{C. and } 76 \text{ cm.}$$

of mercury.

This is a perfectly general relationship and may be represented by

$$V_0 = V_1 \times \frac{P_1}{P_0} \times \frac{T_0}{T_1} \qquad (5)$$

We may then calculate the volume of any given sample of gas at any desired condition of temperature and of pressure from its volume at any other temperature and pressure by multiplying the given volume first by the ratio of the pressures and second by the ratio of the absolute temperatures. In

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tion to standard conditions by using the
ich is easily derived from equation (5)

$$V_0 = \frac{V_1P_1}{76\,(1 + 0.00367t)}$$

which t is the Centigrade temperature at wh
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ther Physical Properties of Oxygen.—Sol
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nething like 10 times its own volume of oxy
rt of which it gives off on cooling. The esc
tuberances of silver to grow out from the be
phenomenon known to assayers as sproutin

iquid Oxygen.—If oxygen under atmosph
led below −182.5°C. it becomes a pale bl
a density of 1.12 and boils under atmosp

but is lower if the temperature is lower, the liquid appears. At ordinary temperatures or at any temperature higher than −118.5°C. it is not possible to liquefy oxygen by any pressure however great.

All other gases behave as oxygen does in this respect. Each gas has a certain temperature above which it is impossible to liquefy it. This temperature is called the **critical temperature,** and the pressure which will be just great enough to bring about the liquefaction at the critical temperature is called the **critical pressure.** In the case of oxygen, the critical temperature is −118.5°C. and the critical pressure is 50.8 atmospheres. An atmosphere is a pressure equal to 76 cm. of mercury. For other gases, the critical constants are different, and are characteristic for each substance. In learning the properties of any given gaseous substance, a fairly definite notion of its critical constants and boiling-point should be obtained.

Air is a mixture of approximately one part by volume of oxygen and four parts by volume of other gaseous substances, chiefly nitrogen. Liquid air has something like the same composition but is a little richer in oxygen because this is more easily liquefied than the nitrogen. If the liquid air be allowed to boil away, the nitrogen will come off in relatively greater quantities than the oxygen and the liquid will gradually become richer and richer in oxygen, and finally will yield a gas containing 95 per cent. or more of oxygen. This is the basis of the most important method for the preparation of oxygen upon a commercial scale. The gas is put upon the market in strong steel cylinders under a pressure of 100 atmospheres.

Both gaseous and liquid oxygen are attracted by a magnet although the attracting force is very much smaller than that exerted upon an equal weight of iron.

Solid Oxygen.—When oxygen is cooled with liquid hydrogen, it freezes to a light blue solid which melts at − 227°C.

Chemical Properties.—The ability to support combustion to an extraordinary degree is the chief chemical property of oxygen, and is made use of in its identification by introducing into some of the gas a glowing spark on the end of a stick, when it at once bursts into flame. This is the test or reaction for oxygen and the splinter or spark is the reagent.

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takes place increases very rapidly until finally the substance kindles into flame. It is not possible to locate very accurately this temperature at which kindling into flame takes place as it depends upon many factors, such as the state of subdivision of the substance, etc. Still less is it possible to locate a temperature above which a substance will combine with oxygen, while below it the reaction will not take place. The rate simply becomes smaller and smaller as the temperature falls. We therefore must conclude that all combustible substances combine with oxygen at all temperatures, although the rate may be immeasurably small.

The combination of oxygen with a combustible substance at temperatures below the kindling point is called **slow oxidation.** This is not essentially different from combustion, and with rising temperature gradually merges into the latter. As much heat is given off during slow oxidation as during the rapid combustion of the same quantity of the substance. If this heat is retained and goes to raise the temperature of the body, as for example, when the reaction takes place in the midst of a heap of coal, the temperature may rise high enough for the substance to burst into flame. When this happens we say it is a case of spontaneous combustion.

Quantitative Relations.—If we study with care the decomposition of mercuric oxide, taking into account the weights of the various substances, we will find that the weight of the oxygen formed plus that of the mercury is just equal to the weight of the mercuric oxide taken. This shows, of course, that nothing else than mercury and oxygen is formed from mercuric oxide. We will find too that, no matter how or where the mercuric oxide is prepared, there will always be a constant ratio between the weight of the mercury and the weight of the oxygen obtained by decomposing mercuric oxide. This ratio is also the same as that in which the mercury and oxygen combine to form mercuric oxide.

This is simply one example of the law of constant or definite proportions, which is one of the most important of the laws of chemistry, and may be stated as follows: "*Whenever two or more substances combine to form another substance, they do so in a perfectly fixed and invariable ratio by weight.*"

Elements.—As we have seen above, mercuric oxide yields tv substances, oxygen and mercury, whose combined weights a equal to that of the mercuric oxide, while their individu weights are less. This was spoken of as decomposition, and is a common characteristic of all decomposition processes th substances are produced whose individual weights are less th the weight of the substance from which they were formed. we examine the chemical transformations which oxygen unde goes, we will find that in no case is there a substance forme whose weight is less than that of the oxygen used up. In or case, that of the formation of ozone (p. 29), the weight (the resulting substance is the same as that of the oxyge consumed; in all other cases it is greater. We must conclu then that oxygen has never been decomposed, that is, change into something having a smaller weight. The same is true f mercury, and for about 80 other substances. *These substanc are called the elements,*[1] *and in all ordinary chemical transform tions they yield substances of either equal or greater, but never le weight than their own.*

Many of these elements are familiar from our contact wi them in every-day life; for example, oxygen, mercury, sulfu iron, copper, lead, gold, silver, carbon, tin and zinc. A cor plete table of the elements may be found on p. 79.

Compounds.—These elements are capable of entering in combination with one another, thus giving rise to the almo innumerable substances known to chemists as chemical cor pounds. These chemical compounds show the following cha acteristics. They have entirely different properties from tho of the elements from which they are formed. They are hom geneous. The proportions by weight in which the elemen combine is in accord with the law of constant proportions. Tl weight of the compound is always greater than that of any o of the elements from which it was formed and is equal to tl sum of their weights. Probably the most important of ε properties is that described by what is known as the *law of t conservation of the elements. No ordinary chemical process* (e

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[1] The word "ordinary" is introduced here to exclude radio-active tran formation, since it is possible that in these cases the above statement m not hold.

cluding radio-active changes) ever produces from a compound any other elements than those which united for its formation, and these elements are reproduced in precisely the proportion by weight in which they combined for the formation of the compound. These points may be illustrated by mercuric oxide. It may be formed by the union of the two elements oxygen and mercury in definite proportion by weight. Its properties are very different from those of mercury and of oxygen, and no elements but mercury and oxygen have been obtained from it. With a proper understanding of the meaning of the term "element," we may now resume the discussion of the element oxygen.

Occurrence in Nature.—As we have already seen, oxygen makes up about one-fifth of the volume of the air. That the air is a mixture of gases and not a chemical compound will be shown later. An element which is found in nature uncombined chemically with any other elements, although it may be mixed with them, is said to exist in the "free state." Since there is such a great quantity of air, oxygen in the free state is very plentiful. The compounds of oxygen are numerous and exceedingly abundant. More than 47 per cent. of the earth's crust and eight-ninths of the water is oxygen.

Almost every one of the elements is capable of undergoing chemical change with oxygen. Each substance so formed differs radically in its properties from either oxygen or the other element. Its weight is equal to the sum of the weights of the other element and of the oxygen, and the two elements unite for the formation of the substance in perfectly definite proportion by weight. Therefore all substances formed in this way are chemical compounds, and since they all have one common component, oxygen, they are called oxides. We have, for example, oxide of mercury, oxide of iron, oxide of lead, etc.

Preparation of Ozone.—When oxygen is exposed to the influence of the silent electrical discharge, (Fig. 6) it undergoes remarkable alterations in its properties, and is partially transformed into a new substance called ozone. By removing the latter as it is formed, the whole of the oxygen can be changed into ozone.

Physical Properties of Ozone.—When oxygen is converted into ozone, the volume of the ozone is only two-thirds that of the

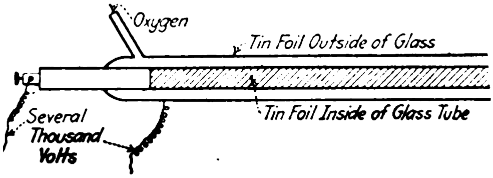

FIG. 6.

hemical Properties.—Gaseous ozone has
on on the mucous membrane. A piece of
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when exposed to the action of ozone
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veight of ozone

water, and in addition is used for the purification of air and of starch, resinification of oils, and in the aging of liquors. Its use for the purification of air is of somewhat doubtful value, since to destroy bacteria in air the ozone must be strong enough to kill guinea pigs and in this strength would in all probability be dangerous to human beings.

Allotropy.—Oxygen may be converted into ozone or ozone into oxygen without any alteration in weight. From this the conclusion is drawn that no other substance combines with the oxygen for the formation of the ozone. This conclusion is confirmed by the fact that when phosphorus is acted upon by ozone in one case and oxygen in another, the same substance, phosphorus pentoxide, is formed in each case, and if equal weights of oxygen and ozone are taken, the weight of phosphorus pentoxide formed in each experiment will be the same. What then is the difference between oxygen and ozone?

Whenever oxygen is transformed into ozone, energy is taken up; and when the ozone is changed back into oxygen, this energy reappears, generally in the form of heat.

Ozone then is to be regarded as a modification of the element oxygen, possessing more energy than the latter. This property which oxygen has in common with several of the other elements of existing in two or more distinct forms, each having its own set of properties, even when the physical state of the different forms is the same, is called allotropy.

Allotropy then is the property shown by certain elements of existing in more than one distinct form, each having the same physical state but possessing different properties. The different forms are spoken of as allotropic modifications of the element.

The fundamental difference between the allotropic modifications of any one element consists of a difference in energy, although in some cases, and possibly in all, there is a difference in molar weight (see p. 68).

CHAPTER IV

HYDROGEN

Hydrogen was shown to be a distinct substance by Cavendish in 1766. It had been observed as an inflammable gas many years before, but was confused with other inflammable gases. That it is an element is shown by the fact that whenever it undergoes chemical changes the substances produced weigh more than the hydrogen which was transformed. Like oxygen it is a gas at ordinary temperatures.

Occurrence.—Hydrogen occurs free in nature in rather small quantities. It is found in the gases given off from some volcanoes and fumaroles and is present in the air to the extent of something like one volume in 30,000 volumes of air. The quantity is so small that it is difficult to determine it with accuracy. In the combined state it is very abundant. Its chief compound is water, of which it forms 11.19 per cent. by weight, the remainder being oxygen. It occurs also in combination in coal, petroleum, natural gas, and in almost all substances of animal or vegetable origin. It is the essential element in a large and important class of substances known as the acids.

Preparation of Hydrogen.—Since water is so abundant and contains so much hydrogen it would seem natural to suppose that hydrogen might be obtained from it economically by some such process as was used in the preparation of oxygen.

The preparation of oxygen from its compounds is comparatively simple because there are several compounds, for example, mercuric oxide and potassium chlorate, which will break up on being heated to a moderate temperature into gaseous oxygen and some other substance which is either liquid (mercury) or solid (potassium chloride) at ordinary temperatures, and can consequently be readily separated from the gaseous oxygen.

In the case of hydrogen, neither water nor any other compoun has these properties and, therefore, a different method of preparation is required. At a fairly high temperature, water partially decomposed into hydrogen and oxygen, but there s no practical method for the mechanical separation of these two gases. However, if there were present in the heated steam something with which the oxygen in the water vapor could combine to form a compound which is either solid or liquid at ordinary temperature, it ought then to be possible to separate this compound from the hydrogen and so get the latter in the pure state.

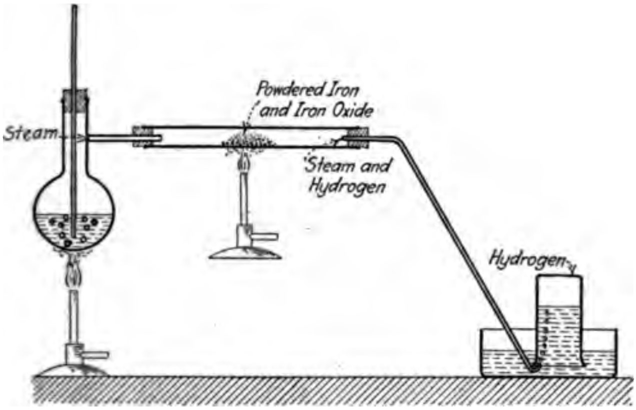

Fig. 7.

Metallic iron forms a compound with oxygen which is solid even at very high temperatures, and if steam be passed over finely divided iron, heated to redness in a tube (Fig. 7) iron oxide and hydrogen will be formed. The iron oxide will remain in the tube, while the hydrogen, mixed with much unchanged steam, will pass on over. The hydrogen may be collected by the displacement of water, as was done with oxygen, the steam which accompanies it being condensed in the water of the pneumatic trough.

The place of the iron may be taken by several other metals. Magnesium, for example, may be used, in which case the temperature may be very much lower. In fact magnesium will rapidly decompose boiling water if a little of a magnesium salt is dissolved in the water to keep the surface of the magnesium free from the magnesium compound formed.

Metallic calcium in the form of turnings decomposes cold water at a convenient rate, thus furnishing a ready n for the preparation of hydrogen on a small scale.

The metals sodium and potassium act upon water so vigoro even at ordinary temperatures, that only very small quan of the metals can be brought in contact with water wit giving rise to dangerous explosions. These methods co essentially in co ound of hydrogen, water, some other ele o ines with the rest of the pound other and leaves the hydrogen These are exar most commonly used met for the prepar nts from their compound

In each of t n and a non-gaseous subst result from the non-gaseous substance con the metal and addition it sometimes con some hydrogen as ter.

Preparation from Acids.—As has been stated above, hy gen is present in all acids. As examples of acids may be

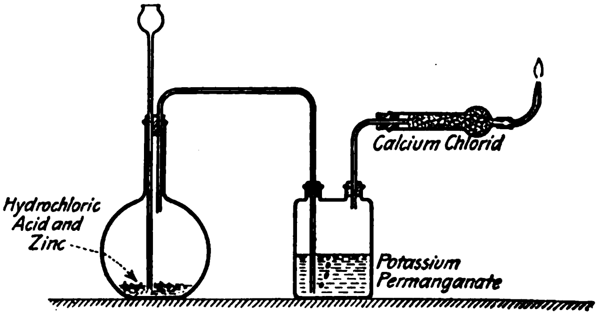

Fig. 8.

tioned sulfuric, hydrochloric, acetic acids, etc. When are mixed with water and brought in contact with many m hydrogen is given off, and each metal forms a compound wit rest of each acid. The hydrogen in each case comes from the and not from the water. Although most metals and acid work in this way, in some cases the action may be viole others extremely slow. Metallic zinc with either dilute su or hydrochloric acid works very regularly and at a conve rate, hence these substances are largely used in the labor for the preparation of hydrogen (Fig. 8).

lrogen is similarly prepared on a commercial scale or for balloons by the action of sulfuric acid on iron, but the ways contains some carbon, and the hydrogen obtained in ıanner is contaminated with compounds of hydrogen and ı.

:trolytic Preparation.—When two pieces of platinum, a which is very resistant to chemical action, are placed in containing a little sulfuric acid, and connected to a suitable : of electricity, a current of electricity passes through the sulfuric acid from one piece of platinum to the other. At ıme time, free oxygen appears at one of the platinum plates :ee hydrogen at the other. The process is really quite com- but since the water gradually disappears and hydrogen and :n appear in the proportion in which they will form water, the quantity of sulfuric acid in the solution is unaltered, it nts to the decomposition of water at the expense of electrical y. Here water is decomposed with the absorption of ical energy very much as mercuric oxide is decomposed at temperature with the absorption of heat, which it will be nbered is a form of energy. Since the hydrogen and the :n are given off at different points, it is an easy matter to t each separately. One of the methods for the commercial ration of hydrogen is based upon this principle using, ver, plates of lead instead of the very expensive platinum. ution of sodium hydroxide may be used instead of the sul- acid, but in this case the metal plates should be of iron or l.

:ification of the Hydrogen.—The hydrogen prepared by the ›ds outlined above always contains water vapor, and usually ›unds of hydrogen and carbon from the carbon contained : metal. The hydrocarbons may be largely removed by ıg the gas through a solution of potassium permanganate. nove the water vapor, advantage is taken of the fact that are several substances which vigorously retain water while ; no action upon hydrogen. One of the most convenient :se is granulated calcium chloride. This is a white, very ›copic substance which is formed as a waste product in chemical operations and is therefore cheap. The calcium le is usually placed in a tube through which the gas is passed. The column of calcium chloride should be as long as convenient and held in place by plugs of cotton wool (Fig. 8).

Concentrated sulfuric acid is a far more efficient drying agent than calcium chloride and is largely used. Since this is a liquid it is either placed in a suitable container and the gas bubbled through it, or it is t [illegible] ce stone and packed in drying tubes or towers.

Physical Properti [illegible] has no taste or color. The pure gas has no od [illegible] pared by the action of acids upon metals usuall [illegible] able odor due to the compounds of carbon [illegible] hich have been mentioned above. After the g [illegible] ssed through a solution of potassium permang [illegible] r purified that it loses the greater part if not a [illegible]

Its density is smaller than that of any other known substance, being 0.00008986 grm. per cubic centimeter under standard conditions. This is perhaps the most important physical property of hydrogen, since upon it depends its use in balloons. The density of pure dry air under standard conditions is 0.001293 grm. per cubic centimeter or 0.0012031 grm. per cubic centimeter more than the density of hydrogen, consequently 1 c.c. of hydrogen under standard conditions will have an upward flotation of 0.0012031 grm. when surrounded by air under the sam conditions.

The extreme levity of hydrogen may be easily shown by fil ing a small rubber balloon with the gas when it will float in th air and exert a lifting power of something like a gram per lite Or soap bubbles may be blown with the gas, and these upon bein detached from the pipe will rise rapidly.

Another way to demonstrate this same property is to fill tw cylinders with hydrogen and hold one of them mouth upward an the other mouth downward. After a few minutes bring a flam to the mouth of each jar. It will be found that the one with th mouth upward contains only air, while the one with the mout downward still contains hydrogen since the gas burns.

Diffusion.—Because of the very great difference in densit between hydrogen and air one would expect that if two cylinder were brought together mouth to mouth (Fig. 9*a*) the upper on filled with hydrogen and the lower one with air, that the gase would remain unmixed. But if they are left in this position for a few hours it will be found that both cylinders contain hydrogen and air. If the cylinders are of the same size and have been left in position for a sufficient length of time, the upper cylinder will contain as much air as the lower, and the lower will contain as much hydrogen as the upper. This spontaneous mixing of one gas with another, even against the action of gravity, is an example of the phenomenon called diffusion.

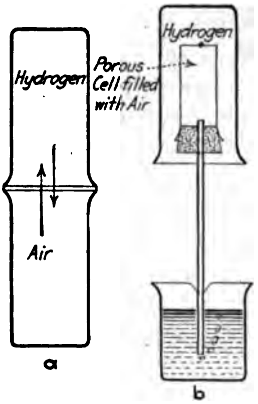

Fig. 9.

All gases diffuse into one another and the process goes on until each gas is uniformly distributed through the entire space. If the pressure of each gas be measured separately, it will be found that diffusion continues until the pressure of any given gas is the same in all parts of the space; and further, it will be found that the pressure exerted by each gas is the same as that which the given mass of the gas would have exerted if it alone were occupying the entire space. This pressure is called its partial pressure. The total pressure of a gaseous mixture is the sum of all the partial pressures of its component gases. The volume of each gas is the total volume of the space occupied by the entire gaseous mixture.

The law which describes these phenomena is known as Dalton's law of partial pressures, and may be stated as follows: *Each gas, in a gaseous mixture, pervades the entire space occupied by the mixture and exerts a pressure equal to that which it would give if it were the only gas present; and the total pressure of the mixture is the sum of these partial pressures of the component gases.*

This law may be expressed in symbols by representing the total volume by V, and that of the separate gases by v_1, v_2, v_3 . . . and the total pressure by P, and the partial pressures by p_1, p_2, p_3, . . . then,

$$v_1 = v_2 = v_3 = V$$

and

$$p_1 + p_2 + p_3 = P$$

While any gas will diffuse into any other gas no matter what the difference in density may be, there is often a great difference in the velocity with which the diffusion takes place. For example, in the case of the hydrogen and air cited above, the hydrogen diffuses downward more rapidly than the air diffuses upward. In fact in all cases the less dense gas will diffuse more rapidly than the dense [illegible]

Something very nea [illegible] nay be demonstrated qualitatively by closing a [illegible] Fig. 9b) such as is used in electric batteries, wit [illegible] ng a glass tube, and supporting the whole arrang [illegible] way that the glass tube dips into water. If a cyli [illegible] g hydrogen be brought over the porous cell, bubble [illegible] begin to pass out from the glass tube. This action [illegible] and if the jar of hydrogen be removed the water [illegible] to ascend the tube. Both effects are due to the fact that the hydrogen being less dense will pass through the porous cell more rapidly than the air, producing in the first case, some little pressure within the cell, and after the removal of the cylinder, the hydrogen passes out so much more rapidly than the air can enter that a partial vacuum results and the water rises.

The relation between the velocity of diffusion and the density is that the velocities of diffusion vary inversely as the square root of the densities of the gases.

Representing the velocities of diffusion by c_1 and c_2 and the density by d_1 and d_2 this relation may be expressed by the equation

$$c_1/c_2 = \sqrt{d_2}/\sqrt{d_1}$$

Hydrogen and the Gas Laws.—The gas laws which were developed under oxygen describe very accurately the behavio of hydrogen under ordinary conditions; in fact, hydrogen follow them more closely than almost any other known gas. At ver high pressures, however, it is found that hydrogen does not decrease in volume as rapidly as it ought according to Boyle's law. The discrepancy becomes greater as the pressure is increased. Other gases at ordinary temperatures are usually more compressible at a moderate pressure than they should be from Boyle's law, and then at higher pressures they behave ıydrogen and become less compressible. At higher tempera- ı many of them act like hydrogen and are less compressible the start than they should be from Boyle's law. At low temperatures hydrogen changes its behavior and is more and then less compressible than it should be, thus ıving like the other gases.

quid Hydrogen.—Hydrogen cannot be liquefied by any sure, however great, at ordinary temperatures, but must be cooled to its critical temperature, −242°C., when it will efy under a pressure of 13 atmospheres. Its boiling-point er atmospheric pressure is about −252.5°C. or only 20.5°A. reducing the pressure to 5 cm. of mercury the temperature to about 14°A. or −259°C. At this temperature hydrogen transparent solid. Liquid hydrogen is colorless and has a ity at its boiling-point of only 0.07. It is used to get very temperatures, since substances placed in it will be very kly cooled to the boiling-point of hydrogen. At this tem- ture all other liquids and all other gases except helium me solids.

olid Hydrogen.—Solid hydrogen is a transparent ice-like tance with a melting-point of −258°C. Its density is 0.076.

bsorption of Hydrogen by Metals.—Hydrogen is absorbed in reciable quantities by many metals, but especially by the metal palladium. Under favorable conditions, palladium take up 900 times its own volume of hydrogen, considerable being evolved during the process. This hydrogen will tically all be given up in a vacuum at ordinary temperatures may be driven off at atmospheric pressure by warming the adium.

he absorbed hydrogen does not enter into a chemical com- nd with the palladium but forms a solid solution.

pectrum of Hydrogen.—When an electric discharge is passed ough hydrogen under a pressure of a few tenths of a centimeter nercury, the hydrogen glows and gives out light. This light ears rose red to the eye, but when it is examined with a troscope (Fig. 10), a very large number of lines are seen tered all along from the red to the violet end of the spectrum. re are, however, four lines, red, green, blue and violet, which much stronger than the others. Other gases under similar conditions will give spectra but no other gas will give lines i precisely the same position in the spectrum as the hydroge lines. These same lines will appear when hydrogen is caused glow in any other way and their appearance is not prevented t the presence of other substances. Hence an examination of tl spectrum is the surest means for the identification of hydr gen. These same lines are found in the spectra of many of tl stars, and we may safely sa that hydrogen is present c them as well as upon the eart (see Frontispiece).

FIG. 10.

The light from the sun an many of the stars shows dar lines at exactly the poin where the hydrogen lines ar bright. As will be explainec p. 293, these dark lines are du to hydrogen, and prove the presence of this element just a certainly as the bright lines. Therefore the spectroscope show us that hydrogen is very widely distributed throughout ou universe. In much the same way it has been established tha a large number of the elements known to us here are also pre ent in the sun and stars.

Chemical Properties of Hydrogen.—The most marked propert of oxygen is that it will support combustion vigorously. Hydr gen on the other hand will burn but not support the combustio of things which will burn in the air. This may be readil shown by bringing a lighted candle to the mouth of an inverte cylinder filled with hydrogen. The gas will take fire with slight explosion and burn with an almost invisible flame at th mouth of the cylinder. Pass the candle up into the hydroge and it will go out. Withdraw the candle slowly, and as th wick passes through the flame of the burning hydrogen it wi be relighted.

From what we have learned of combustion in studying oxyge we would draw the conclusion, correctly, that hydrogen wi combine with oxygen. It will also enter into combination wit a large number of the other elements—notably with chlorin sulfur, nitrogen, and carbon. The conditions under which th combination will take place, and the substances formed will be discussed in connection with the several elements.

A small stream of hydrogen issuing from a jet of platinum, or other difficultly fusible metal, burns quietly in the air with an intensely hot flame which is almost invisible. If the jet is made of glass the hydrogen flame will be colored yellow from the sodium of the glass. Water is produced by the burning of hydrogen, as may be shown by holding a glass cylinder over the flame. A dew at once appears on the glass which has all the properties of water and consequently is water. If all the water formed by the burning of a given quantity of hydrogen be collected and weighed, it will be found to weigh much more than the hydrogen itself, and therefore it follows that water is a compound of hydrogen with one or more of the constituents of the air.

If the air be replaced by pure oxygen it will be found that the hydrogen will burn even more vigorously and water will be produced as before. Hence we must conclude that water is a compound of hydrogen and oxygen and nothing else, a conclusion which is confirmed by the fact that the weight of the water formed is equal to the sum of the weights of the oxygen and hydrogen transformed.

Hydrogen and oxygen may be mixed at ordinary temperatures and no perceptible combustion will take place, but if the mixture be brought in contact with a flame or heated at any point to a temperature of about 500° to 600°C. a combination will take place very rapidly, and a flame will spread throughout the mixture almost instantaneously. The result is a rather powerful explosion due to the sudden expansion of the gases by the heat evolved during the rapid burning of the hydrogen. Because of its explosiveness, a mixture of hydrogen and oxygen in the proportion for the formation of water, *i.e.*, two volumes of hydrogen to one volume of oxygen, is called detonating gas. This detonating gas must be very carefully kept away from flames or incandescent bodies.

Because of the oxygen in the air a mixture of hydrogen and air in proper proportions is decidedly explosive. On this account hydrogen from a gas holder or from a generator should never be lighted until it has been tested and found to be pure. This may be done by collecting the escaping gas in an inverted test tube and bringing it in contact with a flame which is kept at a distance of several feet from the hydrogen apparatus. At first the gas in the tube will behave like air, but soon it will take fire, and the flame will rush up the test tube with a whistling noise. As the trials are repeated and the gas becomes more nearly pure hydrogen, the explosions in the test tube first become stronger and then weaker until at last [illegible] urns quietly at the mouth of the test tube for a s [illegible] time so that a flame may be carried back in this [illegible] rner to the hydrogen apparatus and ignite the es [illegible] s. [illegible] his method of lighting a jet of hydrogen is perfe [illegible] long as the gas in the apparatus is explosive the [illegible] place the instant the mouth of the test tube is br [illegible] ame, and no fire is left in the tube to ignite the jet up [illegible] n of the tube.

Oxy-hydrogen Blowpip [illegible] important applications have been found for the very high temperature produced by hydrogen burning in oxygen. Because of the dangerously explosive character of a mixture of these gases it is of course out of the question to mix them in one gas holder and burn the mixture. The gases must then be stored separately and burned from a special burner called the oxy-hydrogen blowpipe (Fig. 11) which is so arranged that the gases are conveyed to the burner in separate tubes and mixed just before they reach the orifice of the burner. In this way a flame may be produced whose temperature is something like 2,500°C. In this flame silver boils, iron burns, and even platinum melts. If the flame be brought in contact with a piece of lime the latter becomes intensely heated and produces an exceedingly bright light known as the calcium light, or lime light, and has often been used as a source of light for the stereopticon, but is now generally replaced by the electric arc or the nitrogen filled tungsten lamps. The oxy-hydrogen blowpipe is largely used in the autogenous welding of metals, especially of lead.

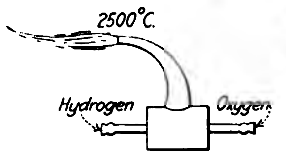

FIG. 11.

Formation of Water from Hydrogen and Oxygen Compounds.—If hydrogen be passed over mercuric oxide at ordinary temperatures no perceptible action takes place, but if the oxide be gently warmed taking care that the temperature does not rise high enough to bring about its decomposition, water and metallic mercury will be rapidly formed. Hydrogen and iron oxide heated to a somewhat higher temperature will yield water and metallic iron. If tin oxide is used, metallic tin and water will be formed. Many other oxides will react in the same way with hydrogen so that we have here a rather general method for the laboratory preparation of a metal from its oxide.

A very natural inference to draw from these facts is that the hydrogen has a stronger attraction for the oxygen than the metal has, and so robs the latter of its oxygen. This conception has often been used, and the attraction is called chemical affinity. That this conception is inadequate is shown by the following case. Iron oxide and hydrogen will react at a somewhat elevated temperature for the formation of water vapor and metallic iron. And the explanation of this in terms of the above conception would be that the hydrogen had a greater affinity for the oxygen than the iron had. But as was mentioned on p. 33, if water vapor be passed over metallic iron heated to the same temperature used in the above case, hydrogen and iron oxide will be formed. The explanation of this would be that the iron had a greater affinity for the oxygen than the hydrogen had and so robbed the water of its oxygen. The action in the one case is just the reverse of that in the other and of course it cannot be that the iron has both a greater and a less affinity for oxygen than hydrogen has. Nor can the reversal be due to change in affinity due to the difference in temperature because the reactions both take place at the same temperature. From this it can be seen at once that the explanation must be either abandoned or modified.

Such actions as these we have just been discussing are called reversed or reversible reactions and are very common in chemistry. In fact they are more commonly met with than the irreversible reactions or those which go only in one direction. A careful study of these reactions is desirable because of their frequent occurrence, and also the ease with which they may be controlled when once understood.

Probably the best way to obtain an understanding of reversible reactions is to consider them as being composed of substance merely by its presence increasing the rate at which a reaction takes place. (See case of manganese dioxide and potassium chlorate, p. 17.) Some other metals have the same property although to a smaller degree than platinum and it is very common to find that the rate of a reaction is greatly altered by the presence of a substance which is not changed by the reaction. We call [illegible]ind catalytic actions. The substance through wh[illegible] rate of action is altered is called a catalyzer, an[illegible]ess is spoken of as catalysis.

Some catalyzers a[illegible]es in this case and increase the rate of reaction; [illegible]positive catalyzers. Others decrease the rate of r[illegible]nown as negative catalyzers. Catalyzers simply a[illegible] which a reaction is taking place and cannot bring[illegible]ich is not already going on. Cases of catalysis are [illegible]ent occurrence and will be often mentioned in the course of this work.

CHAPTER V

WATER

ater is one of the most important as well as one of the most ly distributed substances in nature. Some idea of its dance may be gathered from the fact that the ocean cons about 300,000,000 cubic miles of water and each cubic weighs over 4,000,000,000 tons. Liquid water covers er cent. of the earth's surface; the atmosphere contains mous quantities of water in the gaseous state, and the polar ns and the tops of lofty mountains are covered with solid r or ice. The crust of the earth is everywhere permeated vater, and all living organisms, both plants and animals,

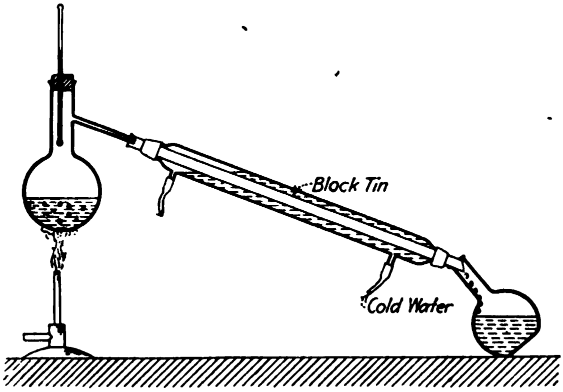

FIG. 13.

ain water as an absolutely essential portion of their struc- . The human body contains about 70 per cent. and the nary foods from 35 to 95 per cent. water.

ater is a very good and general solvent and takes up more ess of nearly everything with which it comes in contact. er is usually purified by the process of distillation which ists in heating the water until it boils and is converted into vapor and then, in a separate vessel (Fig. 13), cooling the vapor and reconverting it into water. Most of the substances present in the impure water are much less easily vaporized than water and are left behind when the latter is boiled. Some impurities, such as ammonia and carbon dioxide, are more volatile than water and pass over with the first portions of the vapor. By rejecting the first part of the dis[illegible] pure water may be obtained. Absolutely pure wa[illegible]pared because it must come in contact with a [illegible]kind, and it will inevitably dissolve some of th[illegible]endering the water impure. Stills and condens[illegible]or pure block tin are least attacked and give [illegible]

For drinking p[illegible]lved impurities in natural fresh waters are not [illegible] as the bacteria which they carry. Since the latter are in suspension and not in solution, they may be removed by very fine-pored filters, and in a sense the water is thereby purified. The same result may be obtained by killing the bacteria by ozone (see p. 30), or by bleaching powder (see p. 129), or by boiling.

Physical Properties of Water.—It is at ordinary temperatures a transparent, almost colorless liquid with a faint bluish tint which becomes apparent upon looking through a thick layer of water. This color can be seen in clear lakes and in the ocean.

Most substances increase in volume more or less regularly with rising temperature, but water is a decided exception. If one starts from 0°C. and warms the water its volume will decrease until a temperature of 4°C. is reached, and then with rising temperature the volume increases. Since the density of a substance varies inversely as its volume, the temperature of maximum density of water is 4°C.

The following table gives some of the values for the density of water at different temperatures:

Temperature	Density	Temperature	Density
0° C.	0.99987	40° C.	0.99224
4° C.	1.0000	60° C.	0.98324
10° C.	0.99973	80° C.	0.97183
20° C.	0.99823	100° C.	0.95838

ce.—At a temperature of 0°C. water changes from the liquid the solid state and is then known as ice. This change is on border line between physical and chemical changes; so ny of the properties of ice are different from those of water, will be seen from what follows, that it may properly be nsidered a chemical change, and yet the transformation back d forth takes place so easily that many regard this as a ysical change.

Properties of Ice.—Ice is a transparent solid of a faint bluish lor which is seen only in large masses such as icebergs or aciers. It is such a poor conductor of electricity that it ecomes electrified when rubbed. Ice is almost twice as good conductor of heat as water, but even then it is a very poor onductor.

The density of ice at 0°C. is 0.91674, which is much smaller han that of water at the same temperature which is 0.99987. This means that on freezing water increases nearly one-eleventh n volume, and also that ice will float on water. In these espects water is somewhat unusual, since most substances lecrease in volume upon solidification, and the solid sinks in the liquid.

In all climates where freezing and thawing take place, the reat increase in volume when the water passes into ice has played a very important part in the disintegration of rocks. When the rain falls upon the rocks it fills even the small cracks. Upon freezing the increase in volume forces the crack to widen. When the ice melts the water runs down in the crack, and upon reezing spreads the pieces of rock still farther apart until resently the rock is split up under the repeated action of the reezing and thawing of the water. The bursting of water pipes when the water in them freezes, and the loosening of the soil n the winter time are due to this same cause.

Ice is a crystalline substance, and crystals may be defined as odies many of whose properties vary with the direction in which they are measured. As a result of this variation a rystalline substance tends, when it takes on the solid state, o form bodies whose limiting surfaces meet at perfectly definite angles, and so build up regular polyhedral forms. All other hysical properties which can possibly do so vary with the direction in which they are measured. Some of these properties are conductivity for heat and electricity, velocity of light, elasticity, etc.

Those solids which are not crystalline are called amorphous substances, and glass is a good example of such a substance. All the properties of glass are the same in every direction. The property of forming r common among pure solid substances, while mo ubstances are mixtures.

Well-formed crysta on the surface of water, but the best are foun w because they have been formed in the air with terfere. The snow crystals usually appear as six-poin

Water in contact with t be cooled below 0°C. nor warmed above this tempe t so long as there is present an intimate mixture of ice a ter the temperature is 0°C. For this reason the ice point is generally used for a standard temperature.

In the absence of ice, water may be cooled a number of degrees below zero without freezing. In this condition it is said to be **supercooled.** It is interesting to note that while water is cooling down from 0° it continues to expand just as it does from 4° to 0°. In fact there is no sudden change in the properties of water at 0° except that at that temperature it becomes possible for ice to exist which it cannot do at higher temperatures. Water which has been cooled to a few degrees below zero is stable toward all kinds of changes except the introduction of ice. Let the very smallest piece of ice come in contact with the water and freezing at once starts and the temperature rises to 0°C.

If a test tube partially filled with ordinary distilled water be supported in a freezing mixture of ice and salt in such a manner that the surface of the water in the tube is a centimeter or so above the surface of the freezing mixture, the water will supercool several degrees. By taking elaborate precautions water has been supercooled to − 15°C.

Heat of Fusion.—Whenever any liquid substance soli heat is evolved; and conversely when a solid melts heat sorbed. The heat absorbed during the melting of 1 grm. solid without raising its temperature is called the heat of of that solid. That evolved during the freezing of unit substance is called the heat of solidification. These heats are equal numerical value and are both often called the heat of ion. Ice behaves like all other solids in these respects and is ly noteworthy because its heat of fusion is greater than that of y other substance except ammonia.

Measurement of Heat.—A quantity of heat is measured by termining the change in temperature which it will produce in a nown weight of water; the heat capacity of the water, *i.e.*, e number of joules required to raise the temperature of 1 m. of water 1°, having been carefully determined. The heat pacity is also known as the specific heat and varies somewhat ith the temperature. Another unit is that quantity of heat hich raises the temperature of 1 grm. of water 1°C. This is alled the small calorie (abbreviated "cal."). Since the specific eat of water varies with the temperature, it is necessary to pecify the temperature of the water. A larger and very generally sed unit is the large or kilogram calorie. It is the heat necessary o rise the temperature of 1 kgm. of water 1°C. It is abbreviated Cal. and equals 1,000 small calories.

The heat of fusion of ice, that is, the heat required to melt 1 grm. of ice, is 334 joules or 80 cal. If, therefore, 80 grm. of water at 1° be mixed with 1 grm. of ice, 81 grm. of water at 0° will be produced.

In technical work in England and the United States, another unit for the measurement of heat is in use. It is known as the British thermal unit and is abbreviated B.t.u. It is the quantity of heat required to raise the temperature of 1 lb. of water 1°F.

The relation between the small calorie and the erg has been carefully worked out by Joule and others, and a small calorie at 15° is equal to 41,880,000 ergs or 4.188 joules.

The fact that the temperature of a mixture of ice and pure water is always 0° finds its explanation in this heat of fusion. If heat is applied to the mixture, instead of raising the temperature some of the ice melts and absorbs the heat. If heat is taken away from the mixture, instead of the temperature's falling some of the water freezes and supplies the heat. Because of the constancy of this temperature ice finds many applications in science. Because of its cheapness, its great heat of fusion, and its rather low melting-point, enormous quantities of ice ar in every day life for the preservation of food since the de tive changes take place much more slowly in the food by ice than at ordinary temperatures. They are like all chemical changes in that they are slowed down by lowerin temperature.

When ice are brought together a sol results, the which is much lower than This is the b e and salt for freezing ice c etc. By usi e to one of salt a temperat −18°C. can was taken by Fahrenheit oint for his thermometer. salt may be replaced by substances because the fre point of any solution is lower than of the pure liquid. Most subst will not give as low a temperatu salt, but a few will give even l However, because of its cheapnes convenience salt is the best to use. use of salt for the removal of ic snow from sidewalks, etc., depends this same phenomenon.

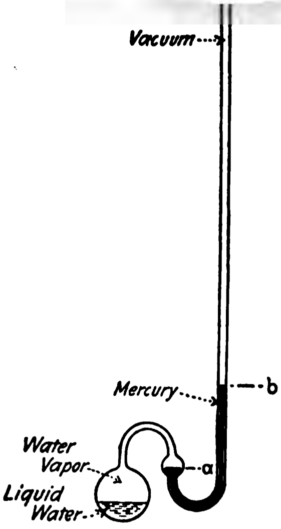

Fig. 14.

Gaseous Water.—Both water a are very easily transformed into ga water which is commonly know water vapor at ordinary and as ste higher temperatures, although th no real difference between them. bring about this transformation, al is necessary is to introduce the wa ice into a vessel which it doe entirely fill. Under these circumst the formation of the gaseous water will begin at once an vapor will soon fill all the space unoccupied by the modification. The transformation of water or ice into vapor is called evaporation. Water vapor is a gaseous stance and its behavior is fairly well described by th laws. This is particularly the case if the pressure is all other gaseous substances, it exerts a pressure upon walls of the containing vessel, and experiment shows when water is brought into a space which it does not fill, oration takes place until either all the water has been erted into vapor or the pressure of the water vapor has ıed a certain definite limit. This limit varies with the ›erature but is always the same at any given temperature, is entirely independent of the shape or size of the vessel ıe relative volume of the liquid or the solid and the water r. We are dealing here then with a state of equilibrium een the water vapor and the liquid water or the ice. The ing pressure at which the water vapor is in equilibrium the other modification is called the **vapor pressure** of the r, or of ice as the case may be. It may be measured in the ratus shown in Fig. 14. The vertical distance from *a* to *b* ures the vapor pressure.

e following table gives the vapor pressure of water at ent temperatures:

VAPOR PRESSURE OF WATER

era- C°	Pressure in cm.	Temperature C°	Pressure in cm.	Temperature C°.	Pressure in cm.
	0.46	25	2.35	70	23.38
	0.65	26	2.50	80	35.55
	0.92	27	2.65	90	52.60
	1.27	28	2.81	95	63.40
	1.74	29	2.98	96	65.77
	1.85	30	3.16	97	68.21
	1.97	40	5.50	98	70.73
	2.09	50	9.22	99	73.32
	2.22	60	14.92	100	76.00

om Dalton's law of partial pressures and the fact that water r is gaseous, it can be readily seen that the vapor pressure of r will be the same whether the evaporation takes place in a um or into a space filled with gases which do not dissolve ıy marked degree in water. If the gases are very soluble will alter the water, and hence the vapor pressure of the r.

When heat is applied to water in an open vessel, the temperature of the water gradually rises and finally small bubbles of gas appear in the liquid, rise to the surface and burst. These small bubbles consist of the gases dissolved in the water and of water vapor. The temperature continues to rise and these small bubbles are replaced by larger ones which consist of water vapor alone. This [illegible]non is then called boiling. After the water has begun [illegible] the temperature does not rise.

A little reflection will convince [illegible]ne that a bubble of vapor down in the body of the liq[illegible]t be under a pressure equal to that of the atmosphere plus [illegible] due to the column of liquid above it, and that due to the [illegible] of surface tension.

The vapor pressure of the [illegible]quid must be equal to these. Neglecting the last two fac[illegible]h are usually small, we may say that *the boiling-point of a liquid is the temperature at which the vapor pressure of the liquid is equal to the atmospheric pressure.* Since the boiling-point is the temperature at which the vapor pressure of the liquid is equal to the external pressure, the boiling-point will vary as the pressure changes, and will rise as the pressure is increased. The boiling-point of water under a pressure of one atmosphere is 100°C.; at two atmospheres the boiling-point is 121°C.; under ten atmospheres it is 180°C., and continues to rise up to the critical point when the boiling-point of water is 374° C. under a pressure of 200 atmospheres. By lowering the pressure, water may be made to boil at temperatures below 100°C. With the aid of a good water vacuum pump, water may be made to boil at temperatures below 30°C. If the pressure be reduced to less than 0.4 cm. of mercury, the boiling-point will fall below the freezing-point, and the water will freeze and boil at the same time.

Use is often made in the laboratory of the fact that the temperature of water boiling in an open vessel, and also the steam from it is never far from 100°C. For example it is often necessary to heat a substance to about 100°C. and at the same time ab lutely essential that the temperature shall not go higher. T can be easily done by heating it on what is known as a wat bath. The simplest form of a water bath consists of a be half full of water and loosely covered with an evaporating or other suitable vessel containing the substance to be heated. If now the water be boiled, the steam will come in contact with the dish and quickly raise the temperature to about 100°C. but never above the boiling-point of water at the pressure of the atmosphere.

Humidity of the Air.—From the very wide distribution of liquid water upon the earth's surface, it of course follows that water vapor is always present in the air. One might expect that the partial pressure of water vapor in the air would be equal to the vapor pressure of the water. However, this is rarely the case because the temperature of a body of water is usually lower than that of the surrounding land area, and even if the partial pressure of the water vapor in the air over the water becomes as great as the vapor pressure of the water at the temperature of the water, as soon as the air moves over the land, its temperature will rise and the partial pressure of the water vapor will then be less than the vapor pressure of the water at the temperature of the air. This is sometimes expressed by saying that the air is only partially saturated, carrying the idea that the air dissolves the water much as water dissolves salt. The notion is only partly correct. The term "relative humidity" is often used in this connection and is the ratio of the partial pressure of the water vapor in the air to the vapor pressure of water at the temperature of the air.

The water vapor in the air is of great consequence in chemistry because of the fact that everything which is exposed to the air takes on more or less water. Some things take on so much water that they pass into a liquid solution or deliquesce, while others simply condense a thin film of water upon their surface. This last is the behavior of glass and other substances that do not dissolve. This water condensed upon the surface often gives a great deal of trouble in making accurate weighings, because of the fact that it will vary markedly with the relative humidity and temperature of the air. The most efficient way to remove this film of liquid water is to heat the object and drive the water off as vapor. However, it must be noticed that a film of water does not behave exactly like liquid water in that its vapor pressure is very much smaller than that of liquid water at the same temperature, and consequently the temperature has to be very high to remove the water thoroughly. In some cases it is nc possible to heat the object to drive off the water, and in this cas it must be placed in a closed vessel called a desiccator whic contains one of the drying agents already mentioned. Unde these conditions, the water will vaporize from the object an slowly diffuse to the desiccating substance. The process is very slow one anc [illegible] astened by removing the air since the latter in [illegible] diffusion of the vapor.

Heat of Vaporiz [illegible] -Whenever any liquid, wate included, passes in [illegible] te heat is absorbed unless th transformation tak [illegible] itical point. This absorptio of heat is not acc [illegible] se in temperature and simpl represents the di [illegible] between the liquid and th gaseous substance [illegible] done in the transformation This absorption of hea [illegible] scribed to the work done i separating the particles of water from each other, since gaseou water occupies a very much larger volume than the liquid wate from which it was formed. However, this cannot be the explana tion because there is an increase in volume when water freeze and yet heat is given out in this case. The heat absorbed in th transformation of 1 grm. of a liquid into its vapor, without ris in temperature, is called its heat of vaporization. In the case c water it is 537 cal. or 2,245 joules at 100°C. or 606.5 cal. or 2,53 joules at 0°C. So as the temperature rises, the heat of vaporiza tion decreases and becomes zero at the critical temperature.

Steam is extensively used for the heating of buildings, becaus such large quantities of heat may be transmitted with th movement of only a small amount of substance.

Effect of Pressure on the Melting-point of Ice.—Ice and wat exist in equilibrium over a certain range of temperature an pressure, for each temperature there is a perfectly definit pressure of equilibrium. Experiment has shown that th melting-point of ice is lowered by 0.0072° for each atmosphere b which the pressure is increased. An increase in the pressure o 139 atmospheres is required to lower the temperature 1°C. A mixture of ice and water then, can have a temperature of 0°C only when under a certain pressure. By definition of 0°C. thi is the standard pressure. A change in the barometric pressu should then affect the melting-point of ice and the alteratio hould amount to about 0.0001°C. for a change in the barometric pressure of 1 cm.

Although the lowering of the temperature for each atmosphere increase of pressure is very small, it is possible by pressure alone to keep water in the liquid state at −24°C. The pressure necessary for this may be most readily obtained by freezing a part of the water contained in a very strong steel vessel. The freezing of only a small part of the water will produce an enormous pressure because of the marked increase in the volume of water when it is changed into ice.

The Law of Mobile Equilibrium.—The melting-point of practically every solid is altered to some extent by a change in pressure. An increase in pressure lowers the melting-point of some few but raises that of most substances. In every case an increase in pressure causes some of the less dense form of the substance to change into some of the denser form, and so produces a contraction which tends to relieve the pressure. To maintain a balance under such conditions between the relative quantities of the two forms, the temperature must be altered in such a direction as will of itself tend to produce more of the less dense form. Usually the solid is denser than the liquid, and the tendency is for it to form when the pressure is increased. So the melting-point of most substances is raised. The case is just the other way around with water for the ice is less dense than the water and the melting-point is lowered. In every instance we are dealing with an equilibrium between a solid and a liquid, and the shifting of this equilibrium under the action of a constraint in the form of pressure. The equilibrium is always shifted in such a way that the pressure tends to be relieved. These are special cases of a very general law which applies to all kinds of equilibria both physical and chemical. This law may be stated as follows: *If a constraint is put upon a system in equilibrium whereby the equilibrium is altered, that reaction will follow which tends to decrease the constraint.*

Solutions.—It is a matter of every-day experience that many substances will dissolve in water. We call these water or aqueous solutions of the substances. A solution, it will be recalled, is a homogeneous mixture of two or more substances, the relative proportions of which may vary continuously within certain limits and whose properties vary with the proportions of the components. Solutions may exist in all three of the physical states, and it is simply the circumstance that we are so familiar with water solutions that makes us tend to think of a solution as a liquid.

In connection with solutions two terms, solute and solvent, are in constant use, and their mea hould be understood. The substance which is dissolved is d the solute, while that in which the solute is dissolved is ca d the solvent. A solution of salt in water is obtained by diss lving the solute salt in the solvent water. The solute may be olid, liquid, or gaseous, and so may the solvent. As an examp of a liquid dissolving in a gas, we may take the vaporization water into air.

Aqueous solutions are of great i rtance in chemistry because of the fact that many chemical processes take place very readily in them; one reason for this being, apparently, that the water will bring together into one liquid, solid, liquid or gaseous solutes in the very most intimate mixture.

In general, solutions have properties which are a sort of mean between the properties of the two components, so these aqueous solutions will have in the main the properties of water. One very important circumstance to note about solutions is that a solute always lowers the vapor pressure of its solvent upon passing into solution. From this it follows that if the solute is nonvolatile, the vapor pressure of the solution will always be less at any given temperature than the vapor pressure of the pure solvent. In case the solute is volatile, the partial pressure of the solvent is lowered as before, but the vapor pressure, which is the sum of the partial pressures of the solvent and of the solute, may or may not be lower than that of the solvent in the pure state. For solutions which are dilute, the lowering of the vapor pressure is proportional to the mass of the solute dissolved in a given fixed mass of the solvent, at constant temperature.

In Fig. 15, the curve AOB is the vapor pressure curve for the pure solvent, and the curve CO′D that for the solution. It will be noticed that the curve for the solution lies below that for the solvent, and that they are not parallel. The curve EO′O is the vapor pressure curve for the ice. The line MN represents the atmospheric pressure. From the definition of boiling-point it will be seen that the temperature corresponding to the points B and D represent the boiling-points of the pure solvent and of the solution respectively. This also shows that owing to the decrease in the vapor pressure caused by the solute, the boiling-point of the solution is higher than that of the solvent. This is true in every case where the solute is non-volatile. If the solute is volatile, the boiling-point of the solution may be higher or lower than that of the pure solvent depending upon whether the partial pressure of the solute is less than or greater than the lowering of the vapor pressure of the solvent.

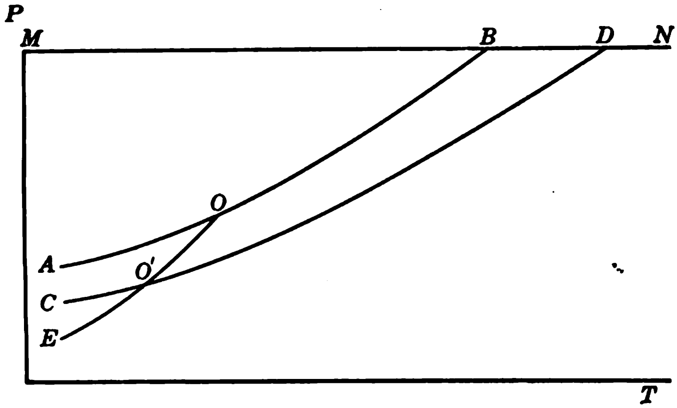

FIG. 15.

The freezing-point of all solutions from which the solvent separates as a pure solid is lower than that of the pure solvent. In order to understand this, it will be necessary to consider the relations between the vapor pressure of the solid and of the liquid. It seems very natural to assume that ice has no vapor pressure, but this is a mistake for ice has a measurable vapor pressure even when cooled to many degrees below zero. This pressure is 0.46 cm. at zero degrees, and becomes smaller as the temperature falls. As may be seen by reference to Fig. 15, the vapor pressure curve for ice is not a continuation of that for water, but lies below the water curve except at point O, where the curves meet. It is only at this point, O, then that the solid and liquid have the same vapor pressure and can be in equilibrium with each other. At temperatures below this point the vapor pressure of the water is higher than that of the ice and a little thought will convince anyone that the two could not continue to exist side by side because the water would evaporate and condense on the ice as the solid, and this would go on until all the water had disappeared. A little reflection will show that a systen quilibrium in every way to be in equilibrium in a refore it follows that since at the freezing-point th e liquid are in equilibrium, the vapor pressure of t m e the same. We may then frame a definition of th it so that it shall be similar to that for the boiling- eezing-point of a substance is the temperature at he pressure of the solid is the same as that of the liq 1. In Fig. 15 this is at the point O, where the two cu d EO′O cut. Correspondingly the freezing-point of the solution will be the temperature at which the vapor pressure of the solution equals that of the ice,[1] and this will be at the point, O′, on the curves and will always be at a lower temperature than that of the pure solvent. From these considerations it will be seen that the solute lowers the vapor pressure of the solvent and that this results in the solutions boiling at a higher, and freezing at a lower temperature than the pure solvent. No real explanation for the lowering of the vapor pressure can be given, but we can picture it to ourselves by assuming that things dissolve because they have an attraction for each other, and that, because of this attraction the solvent finds it more difficult to pass over into the gaseous state from a solution than when it is pure.

When a solid salt is brought into contact with water, some of it dissolves. If the salt is difficultly soluble, like silver chloride, the weight of the salt which a given weight of water, say 10 grm., can take up is very small indeed; but in the case of an easily soluble compound like calcium chloride, the mass which can be dissolved by the same weight of water is very large. However, there is at each temperature and pressure a definite limit to the weight of a salt which a given weight of water will dissolve. A solution in which this limit has been reached, and which is in equilibrium with some of the solid solute, is called a saturated solution. The ratio between the weights of the solute and the solvent in a saturated solution is called the solubility of the solute. It is usually expressed in terms of parts by weight of solute in 100 parts by weight of solvent.

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[1] The student should remember that when a solution freezes the solid which separates almost always consists of crystals of the pure solvent and not of the solution.

As a rule the solubility of a salt is markedly altered by changes of temperature. Generally, but by no means always, the solubility increases with rising temperature. The solubility is very much less sensitive to changes in pressure than to changes in temperature, in fact it requires a change in the pressure of hundreds of atmospheres to make a measurable change in the solubility. So small is the influence of pressure that for all practical purposes it may be neglected.

If less of the salt be added to the solvent than it is capable of dissolving, all will be taken up. The solution is said to be unsaturated because it can still take up more of the salt. If more of the salt be added than the solvent can dissolve, that quantity which corresponds to the solubility will pass into solution and the excess will be left undissolved. The concentration of the salt in solution is absolutely independent of whether this excess be large or small.

Just as a liquid may be supercooled if the solid modification be excluded, so a solution may be prepared which contains more of the solute than corresponds to its solubility if the solid solute is not present. Such solutions are called supersaturated. In the absence of the solid solute, they are stable toward most changes; but when brought in contact with even a very small piece of the solid, all the excess of solute over that corresponding to its solubility quickly separates out in the solid form.

Application of the Law of Mobile Equilibrium.—We must go to the law of mobile equilibrium for information as to the direction of the change of solubility for a given change in temperature or pressure.

This law says that if a system in equilibrium is subjected to a constraint whereby the equilibrium is altered, that reaction will follow which tends to relieve the contraint. If the constraint consists in the addition of heat whereby the temperature of the system is raised, the change which will follow will be accompanied by the absorption of heat. If a salt dissolves in its almost

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The Chemical Properties of Water.—Wat
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water with lime (calcium oxide) to form
h anhydrous

characteristics of chemical compounds, that is, follow the law of definite proportions, differ radically in their properties from their components, etc., so there is no reason for setting up a special class for these substances.

As cases of the behavior of water as a compound of hydrogen and oxygen, we may call to mind the reactions between water and iron, or magnesium, calcium or sodium whereby hydrogen and a compound of the metal with oxygen or with oxygen and hydrogen are formed. It is important to notice in this connection that it is much more difficult to decompose water into its elements than it is such a compound as mercuric oxide; on this account water is called a stable substance.

The Reaction of Sodium and Water.—The action of sodium upon water is so very vigorous that only very small quantities of sodium, a piece not larger than a pea, should be used at a time. Larger quantities are very likely to produce explosions, from the very great volumes of gas and steam liberated, which are as violent as those due to an equal weight of dynamite. When sodium acts upon water, hydrogen and a solution of sodium hydroxide are formed. Sodium hydroxide is a white easily soluble solid which is a highly caustic alkali and hence is often called caustic soda. When sodium hydroxide is exposed to the air, it becomes moist and finally passes into a liquid which is identical in its properties with a strong water solution of the substance and hence is such a solution. The water necessary for the formation of this solution comes from the air. Sodium hydroxide and things like it which take up water vapor from the air and form solutions are called **deliquescent substances.** All such subtances are very freely soluble and have the common characteristic that their saturated solutions give a smaller vapor pressure of water than the partial pressure of the water vapor in the air. If this were not so the substance could not deliquesce. Many of the salts containing water of crystallization decompose readily into their components and give an easily measurable vapor pressure of water. If the partial pressure of the water vapor in the air is less than the vapor pressure of the water from the salt, the latter will decompose and the crystals will fall to powder. The substance is then said to **effloresce.** At any given temperature the vapor pressure of a saturated solution of a substance or that of water from a hydrate is constant, but the partial pressure of the water vapor in the air varies from time to time, so a substance may deliquesce one day, be stable the next, and even effloresce on the day after; its behavior being determined by the partial pressure of the water vapor in [illegible] vapor pressure of the water from the substance.

In ordinary weathe [illegible] loride will deliquesce, and even after the salt has [illegible], the solution will continue to take up water from [illegible] the partial pressure of the water vapor in the air [illegible] the vapor pressure of the solution. If such a s [illegible] wed to stand in the laboratory until winter con [illegible] be found that the water will gradually evaporate [illegible] crystals of calcium chloride with water of crystallization will form. In the depth of winter these crystals sometimes fall to a powder or effloresce. So calcium chloride is both a deliquescent and an efflorescent substance. The explanation being of course that in the summer the partial pressure of the water vapor in the air is high, while in the winter it is low indoors on account of the low temperatures prevailing outside.

The Composition of Water.—Water is, of course, a chemical compound of hydrogen and oxygen and hence from the law of definite proportions the relative proportion by weight in which these elements combine to form water will be fixed and invariable. This proportion is a very important property, not only of hydrogen and oxygen, but also of water.

There are two general methods of procedure for determining the composition of a substance. We may decompose the substance into its elements and determine the proportion by weight in which each is present. This is called analysis. Or we may bring together the elements which go to make up the substance and make the conditions such that they will combine to form the desired compound. By carefully noting just what weight each element disappears in the formation of a given weight of th compound, the quantitative composition of the substance may be determined. This is called synthesis.

For the analysis of water, advantage may be taken of the fact

›d under the discussion of the methods for the prepara- ıydrogen, that when a current of electricity is passed water between two plates of platinum, hydrogen ap- one of the platinum plates and oxygen at the other. process the platinum plates are unaffected, and the ›f the hydrogen plus the weight of the oxygen equals ;ht of the water which disappears, thus showing that ›stances are the only ones formed in the process. By g the gases separately and determin- weights, a quantitative analysis of r may be made. Since the densities ›ses are known, it is not necessary ı them; all that is required is that lumes be measured under known ›s of temperature and pressure), and from these data the volumes andard conditions may be readily ›d. The volumes under standard ›s times the densities of the gases ourse, give the weights of the gases, refore the proportion by weight in ıey combine to form water which ›ult desired.

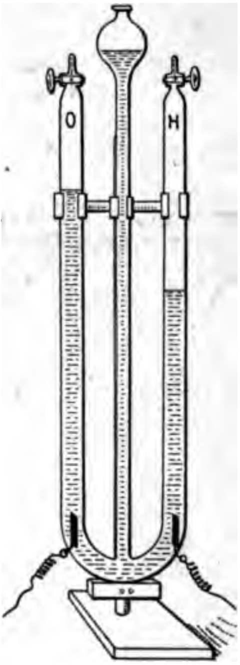

FIG. 16.

this operation is performed it turns ; if the gases be measured under .e conditions of temperature and , that the volume of hydrogen is ›xactly twice that of the oxygen. o according to the best determina- ıng 2.0025 volumes of hydrogen to ›olume of oxygen. The density of ı is 0.00008986 and of oxygen 0.0014293 and therefore ı by weight is 2.0025 × 0.00008986 divided by 1.0000 ×)3, or 1.000 of hydrogen to 7.943 of oxygen or roughly The percentage composition of water is then 11.19 per drogen and 88.81 per cent. oxygen.

: the standard methods which has been much used for the ›tive synthesis of water is based upon the reaction taking ;ween copper oxide and hydrogen at a somewhat elevated temperature whereby water and copper are produced. The process may be briefly outlined as follows: Pure dry hydrogen (Fig. 17), is passed over a weighed quantity of copper oxide at a little below the temperature of redness. The water formed is collected by absorption in a weighed quantity of calcium chloride. The increase in weight of the calcium chloride at the end of the experiment over [illegible] at the beginning gives the weight of the water formed. The ifference between the weight of the copper oxide and of the co per formed from it gives the weight of the oxygen which wa ransformed into the water. The difference between the weig f the water and that of the oxygen is, of course, the weight o he hydrogen. The composition of water from data obtained [illegible] this way checks very closely with that given above.

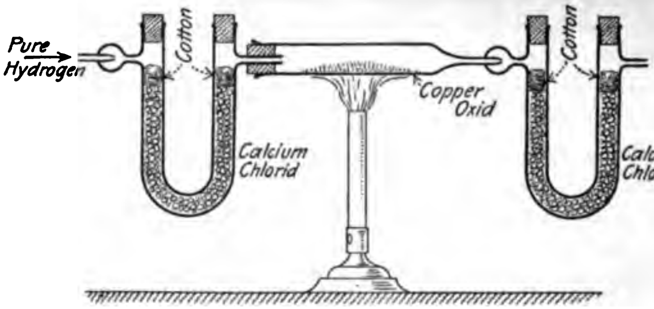

Fig. 17.

Another method for the quantitative synthesis of water consists in determining the proportion by volume in which hydrogen and oxygen unite to form water. From this ratio and the densities of the gases, the proportion by weight may be easily obtained as was shown above. Since a mixture of hydrogen and oxygen may be caused to explode by passing an electric spark through the mixture at any point this synthesis is very easily carried out. The apparatus necessary consists of a thick-walled glass vessel (Fig. 18), strong enough to stand the explosion of the gases and having two platinum wires sealed through its walls. Carefully measured volumes of hydrogen and of oxygen are introduced into the vessel, mixed and exploded. The residual gas is then measured and examined rhether it is hydrogen or oxygen. The results show as ;hat the gases combine in the proportion of very nearly umes of hydrogen to one of oxygen. If the gases are in just this proportion no residue is left; but if an of either one is used, the excess of that gas is left un- l. If this synthesis is carried out at temperatures above ing-point of water and at pressures somewhat below that itmosphere so that the water formed shall stay in the state, as water vapor, the volume of this water vapor nearly the same as that of the n from which it was formed, both d at the same temperature and :. So the following very simple exists between the volumes of the substances involved in this reac- o parts by volume of hydrogen ibine with one part by volume of to form two parts by volume of apor, all being measured under e conditions of temperature and :.

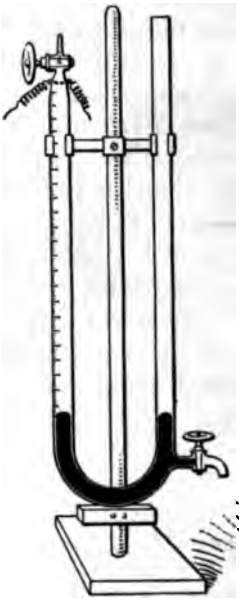

Fig. 18.

ı other gases enter into reaction e another, relations between the ng volumes are always very often even simpler than in the ven above. This behavior of described by the law known as **ssac's law of the combining vol- : gases.** *Whenever in any chem- tion two or more gases appear or ır, they do so in the ratio of small whole numbers by volume.* :ase given above, the ratios are 2:1:2.

ı we come to compare the proportions by volume in olids or liquids react, we find no suggestion of the exist- a simple relation, nor is there any simple proportion by n which substances react. We find here another instance reat simplicity of the behavior of gases.

l be recalled that Boyle's and Gay Lussac's laws do not describe the behavior of any gas, but that they all vary somewhat from these. Similarly Gay Lussac's law of combinin volumes is not an exact law as may be seen from the fact tha hydrogen and oxygen do not combine in the ratio of 2 : 1 as calle for by the law, but in the ratio of 2.0025 : 1. The deviation however, are not large, in most cases, and the law is very usefu and important.

Molar Weight.– [illegible] of molar weights which i about to be develop[illegible] ul since with its aid the inter pretation of many [illegible] plicated chemical phenomen becomes simple.

The molar weig[illegible] se[illegible] substance is conceived of a being proportion[illegible] de[illegible] y of the gas. For reason which cannot be [illegible] l later, the molar weight o oxygen is taken as [illegible] roper point the reasons fo this choice will be given. If then the molar weight of a gas i proportional to its density the following relation will hold:

The molar weight of the gas: the molar weight of oxygen = the density of the gas: the density of oxygen, or

$$\frac{\text{The molar weight of the gas}}{\text{The molar weight of oxygen}} = \frac{\text{The density of the gas}}{\text{The density of oxygen}}$$

Substituting for the molar weight of oxygen its value 32 and solving for the molar weight of the gas, we have

$$\text{Molar weight} = 32 \times \frac{\text{The density of the gas}}{\text{The density of oxygen}} = 32 \times \frac{D}{0.001429}$$

where 0.001429 is the density of oxygen and D that of the g in question.

But $\frac{D}{0.001429}$ is the specific gravity of the gas referred to oxyge Since it is the ratio of the weights of equal volumes (1 c.c. i each case) of the gas and of oxygen. Therefore for a gaseou substance the *molar weight may be defined as thirty-two times th specific gravity of the gas referred to oxygen as the standard.*

For the sake of illustration, let us calculate the molar weigh of hydrogen. The density of hydrogen is 0.00008986, an letting M represent the molar weight,

$$M = 32 \times 0.00008986/0.001429 = 2.012$$

Therefore the molar weight of hydrogen is 2.012.

Water vapor of course cannot exist under standard conditions but could exist at 0°C. if the pressure were less than 0.4 cm. of mercury or at atmospheric pressure if the temperature were higher than 100°C. Since water vapor follows the gas laws, f the weight of a given volume be found under any conditions of temperature and pressure, the density which it would have under standard conditions, if it did not liquefy, can be readily calculated. The density of water vapor obtained in this way s 0.0008063 and hence the

Molar weight of water $= 32 \times {}^{0.0008063}/_{0.001429} = 18.05$.

By a slight extension of the conception of molar weight we can get another very useful conception, that of a gram mole. A gram mole of a substance is nothing more or less than the molar weight of the substance expressed in grams. Or it is a weight in grams of the substance numerically equal to its molar weight. For example, the molar weight of hydrogen is 2.012 and a gram mole of hydrogen is 2.012 grm. of hydrogen. The molar weight of water vapor is 18.05, so a gram mole of water vapor is 18.05 grm. of water vapor. The molar weight of oxygen is 32, and a gram mole of oxygen then is 32 grm. of oxygen.

The volume occupied by a gram mole of a gaseous substance under standard conditions can be easily calculated by dividing its molar weight by its density under standard conditions. The volume of a gram mole of oxygen under standard conditions is then ${}^{32}/_{.00143}$ or 22,400 c.c. The volume of a gram mole of hydrogen is ${}^{2.012}/_{.00008986} = 22{,}400$ c.c. These and other examples which may be worked out, together with a few moments thought on the definition of molar weight should soon convince one that the volume of a gram mole of all gases under standard conditions is the same and is 22,400 c.c.

CHAPTER VI

COMBINING WEIGHTS AND ATOMIC THEORY

There can be no [illegible] n bu [illegible] at the law of combining weig is the most impor[illegible] r [illegible] ion of chemistry, and we m now turn our [illegible] to [illegible]e formulation of this l For this, we shall ne[illegible] nposition of a number of compou as determined by a [illegible] and their molar weights. In or to obtain accura[illegible] is necessary to use not the m weights directly [illegible] the gaseous density, but th plus or minus a s[illegible] ally determined number wh corrects for the deviations of the gases from the simple gas l of Boyle and Gay Lussac. These corrections are easily termined and the corrected molar weights are just as much result of experiment as the uncorrected numbers.[1]

By analysis we get the weight of each element in a gram of compound. If we multiply the weight of an element in a gı of compound by the molar weight of the latter, we obviou obtain the number of grams of the element per gram mole of compound. For example a gram of water contains accord to analysis 0.8881 grm. of oxygen. The molar weight of wat 18.016. If we multiply these two numbers together, we 16.00 which means that 18.016 grm. of water contains 16 g of oxygen.

The following table summarizes this kind of results fo number of compounds, and should be carefully studied, pay particular attention to the weights of each element per gı mole of compound.

The results given in the following table under the headi "weight of each element per gram and per gram mole of c pound," are as described by the law of definite proportions each set represents equally well the relative proportions in which the elements unite to form the compounds. The most careful study of the weights of the elements per gram of compound will fail to shows any simple relation between the weights of any given element, say hydrogen, in the various compounds; but even a very hasty inspection of the weights of the elements per gram mole shows that a gram mole of a hydrogen compound either contains 1.008 grm. or some integral multiple of this number. The same thing is true for oxygen, nitrogen, etc., except that the number is 16 for oxygen, 14.006 for nitrogen, 35.46 for chlorine, and 12 for carbon.

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[1] Some idea of the magnitude of these corrections may be obtained comparing the value for the molar weight of water obtained on p. 69 the corrected value given in the table p. 71 and also that uncorre molar weight of hydrogen 2.012 with the corrected 2.016.

Name of compound	Weight of each element per gram of compound	Corrected molar weight	Weights of each element per gram mole of compound				
			Hydrogen	Oxygen	Nitrogen	Chlorine	Carbon
Water	0.1119 hydrogen 0.8881 oxygen	18.016	2.016	16.00			
Hydrogen chloride	0.0276 hydrogen 0.9724 chlorine.	36.468	1.008	....	.....	35.46	
Ammonia	0.1776 hydrogen 0.8224 nitrogen	17.030	3.024	....	14.006		
Nitric oxide	0.4668 nitrogen 0.5332 oxygen	30.006	......	16.00	14.006		
Nitrous oxide	0.6365 nitrogen 0.3635 oxygen	44.012	......	16.00	28.012		
Carbon dioxide	0.2727 carbon 0.7273 oxygen	44.00	......	32.00	.....	....	12.00
	Minimum weight of each element per gram mole of the compounds.		1.008	16.00	14.006	35.46	12.00

This is true not only for these compounds but also for all other gaseous compounds of these and other elements so that we can make the general statement *that for each element there is a number which represents the minimum weight of that element found per gram mole of any of its compounds, and whenever this element is present in a gram mole of any compound in greater weight than the minimum, its weight may always be represented by an integral multiple of the minimum weight.* These minimum numbers are called the combining weights of the elements because they or their integral multiples represent the proportions by weight in which the elements enter into combination with one another. The statement just given in italics might be c the law of combining weights, but if preferred the follo form may be used. For each element a number can be f which has the property that the proportions by weigh which this element enters into combination with other elem can be represented by this number or some integral mul of it.

No two ele [illegible] same combining weight ar table of these v [illegible] nstants is given on p. 79.

Atomic Theo [illegible] he beginning of the ninete century, the la [illegible] portions (p. 27) was formul and a few yea [illegible] on, an Englishman, discov some of the f [illegible] he law of multiple proport (p. 84) is b [illegible] nsideration of these relat Dalton becam [illegible] s described by the law of c bining weights. He also knew the law of the conservatio the elements. As an explanation of all these facts he ga definite quantitative form to the atomic theory—a theory w had been held by many in some form or other since the of the early Greek philosophers. For the purpose of explai the facts, Dalton made the following assumptions:

First, that all elements are made up of very minute chemic indivisible particles called atoms;

Second, that the atoms of any one element are all alik size, weight, etc., but are very different in all these particu from the atoms of other elements;

Third, that the ratio of the weights of the atoms of any elements is the same as the ratio of their combining weight

Fourth, that compounds are formed by the union of a defi integral number of atoms of one element with a definite wl number of atoms of another to form the smallest particle, ca the molecule, of the compound;

Fifth, that the atoms of any given element preserve t identity in passing from the element to a compound, or f compound to compound.

The explanation of the laws upon which the atomic theor founded in terms of that theory is so simple as to be aln obvious. The fixed relative proportions by weight in which elements unite to form a given compound (Law of Defi

Proportions) is given by the relative weights of the atoms of the elements, each multiplied by the definite integral number of the atoms of that element which united to form a molecule of the compound. Since the atoms are assumed to be indivisible, it follows that in a molecule of any given compound of an element, there will be one, two, three, or some whole number of atoms of that element; and therefore from the relation between the combining weights and the weights of the atoms, the proportions by weight in which the element enters into combination will be represented by the combining weight or some whole multiple of this (Law of Combining Weights). The law of conservation of elements is explained at once by the assumption that the elements preserve their identity in passing from compound to compound. In terms of the atomic theory, what we have called the combining weights of the elements may just as properly be called the relative atomic weights, or simply the atomic weights of the elements. The table on p. 79 entitled "International Atomic Weights" gives the accepted values of these important constants for the elements.

The atomic theory has proved to be one of the most fruitful theories of chemistry, since it not only explains the very fundamentally important laws of chemical combination, but also has brought together a great many other facts and by predicting new relations has led to investigations which have greatly increased our store of knowledge. For a long time there was no proof that substances were composed of particles the size of atoms and molecules; for all elements and chemical compounds when examined under the most powerful microscopes seemed to be perfectly homogeneous. But within the last few years, facts have come to light chiefly by the study of radioactive substances (see p. 496) which seem to indicate very clearly that such small particles do actually exist, and hence the theory has been greatly strengthened. These facts have even enabled us to make a very close estimate of the number of atoms in a gram combining weight or its synonym—gram atomic weight of any element. This number is 6.1×10^{23} atoms.[1] For example 1.008 grm. of hydrogen or 16 grm. of oxygen will each contain $6.1 \text{x} 10^{23}$ atoms.

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[1] 6.1×10^{23} is an abbreviated way of writing 610,000,000,000,000,000,000,000.

This almost inconceivably large number of atoms in a comp
tively small mass of substance enables us to understand f
why it has never been possible to see the atoms.

Molecular Theory.—Just as the atomic theory has proved v
useful in explaining the facts of chemical combination, so
molecular theory has been of help in explaining certain of
other facts of chemistry and physics. Among the facts wh
the theory was devised to explain are those of the behav
of gases, liquids and solids, with changes of pressure and te
perature, and also the relations which we have been consider
under the conception of molar weights.

The more important assumptions made for the purpose
explaining these facts are:

First, that every substance made up of extremely sm
particles called molecules.

Second, that these molecules in the case of compounds
made up by the union of a definite and whole number of ato
of each of the elements composing the compound; in the cas
elements, the molecules may be composed of one or m
atoms—usually more than one;

Third, if anything happens to change the number of atom
a molecule, the nature of the substance is changed;

Fourth, that the molecules behave as though they were exce
ingly elastic bodies in a state of rapid and ceaseless motion
all directions, their rates of motion increasing with rise
temperature;

Fifth, because of their rapid motions, the molecules
assumed to occupy only a very small part of the space whic
apparently filled by the substance which they constitute.
rest of the space being empty. This dispersion of the m
cules is assumed to be especially great in the case of gases, m
less for liquids, and generally still less for solids;

Sixth, it is assumed (Avogadro's hypothesis) that ec
volumes of all gases under the same conditions of tempera
and pressure contain the same number of molecules.

The pressure exerted by a gas is explained as being due to
hammering of the rapidly moving molecules upon the w
of the containing vessel. The latter part of the fourth assu
tion will explain the increase in pressure with rising temperat

if the volume is kept constant; or the increase in volume, if the pressure is unchanged. (Gay Lussac, or Dalton's law.)

Decreasing the volume occupied by a given mass of a gas to one-half its former value will double the number of molecules striking a given area of the wall confining the gas and hence double the pressure. (Boyle's law.)

If Avogadro's hypothesis is true and equal volumes of all gases under the same conditions of temperature and pressure, contain the same number of molecules, then it follows that the weights of these equal volumes will stand to each other in the same ratio as the actual weights of the molecules. We can then by choosing some gas as the standard and assigning to it a certain molecular weight, prepare a system of relative molecular weights of gases which shall have all the properties of that which we have called the molar weights. In fact since oxygen has been taken as the standard and assigned a molecular weight of 32, the numerical values of the molecular weights is just the same as that for molar weights; and a gram mole of a substance is precisely the same quantity of that substance as a gram molecular weight. The expression, molecular weight, is a rather long one, so in accordance with custom, it will generally be replaced in this book by the more convenient word mole.

The same facts of radioactivity (p. 496) which strengthened the atomic theory support the molecular theory and indicate that the number of molecules in a gram molecular weight or gram mole of a substance is the same as the number of atoms in a gram atomic weight—that is to say 6.1×10^{23}. A further strengthening of the molecular theory is furnished by the fact that extremely minute particles, when suspended in a liquid and strongly illuminated, look, when examined by a powerful microscope, like dancing dots of light. The motions of these particles closely correspond in kind and amount to those calculated on the assumption that they are caused by the bombardment of the particles by bodies having the calculated mass and velocity of the assumed molecules.

Relation Between Fact and Theory.—In studying a theory we should always be careful to get thoroughly in mind the distinction between the facts, the assumptions and the explanation. The facts are eternally true. The theory is a speculative explanation of the facts in which our imagination has carried farther than our observations have been able to go. Furtl observations may show that our imaginings (the theory) was a t picture of the way nature works, or they may bring to light n facts which are so out of harmony with what we had imagin that we have to abandon our former theory and invent an e tirely new expla ll at the same time cover t old and the new is last condition has been t usual one in the ry of science shows a great p of discarded theo ese was a good theory in its d because it explai facts and thus simplified an coordinated our lso predicted the existence other facts and s estigation with the result th our field of infor tly extended. Judging fro the past we have e on to expect that the future w replace many of our present theories by better ones. The onl difficulty about a false theory is that if it is too firmly believe in, it blinds one to obvious facts and causes others to be mi understood, and so hinders the progress of science.

The way to use a theory is to keep constantly in mind th it is not a fact and possibly is not true, but to follow up all t lines of investigation which it suggests, always being ready t discover that the facts do not agree with the theory. In particula one should never hesitate to try a thing which upon oth grounds promises success simply because a theory predic failure.

Standard of Atomic Weights.—Our recently acquired know edge of the number of atoms in a gram atomic weight wou enable us to prepare and use a table of the absolute values of t atomic weights instead of that given on p. 79, but these numbe would be long decimal fractions with from 21 to 22 ciphers befo the significant figures, and hence would be far less convenient th our present system which like that for molar weight is entire relative, and therefore necessitates the arbitrary choice of standard. At first, hydrogen was taken as the standard becau it has the smallest combining weight, and was given the relati weight of 1; but of recent years it has been decided that oxyg with a relative weight of 16 is the better standard. One of t principal reasons for this change to oxygen is that many elemen do not form easily volatile compounds so that it is very difficult to determine their combining weights from their minimum weight per gram mole of gaseous compounds. Under these conditions, it is necessary to determine the proportions by weight in which the element of unknown atomic weight will combine with one for which this constant is well known—preferably the standard.

Now hydrogen does not form stable compounds with many of the other elements, while oxygen does. Therefore oxygen is the better for a standard substance. Of course the weight of an element which will combine with 16 grm. of oxygen will not give us directly the atomic weight of the element unless just one atom of it combines with one atom of oxygen; but in any event the weight per 16 grm. of oxygen bears some very simple relation to the atomic weight—*i.e.*, it is twice the atomic weight if two atoms of the unknown combine with one of oxygen, or one-half it if two atoms of oxygen combine with one atom of the other. There is a rather inexact law known as that of Dulong and Petit which states that the product of the atomic weight of a solid element and its specific heat expressed in calories is approximately equal to the constant 6.2. The deviations from this number are rather large, especially for the non-metallic elements of low atomic weight, but in nearly all cases, the value of the atomic weight obtained by determining the specific heat and dividing this into 6.2 is nearly enough correct, so that it will enable us to determine the real value, from the weight which will combine with 16 grm. of oxygen. For example, the specific heat of magnesium is 0.245 and this divided into 6.2 gives 25.3 as the approximate atomic weight of magnesium. But 24.32 grm. of magnesium will combine with 16 grm. of oxygen and therefore the atomic weight of magnesium must be 24.32. For silver the case is a little more complex. The specific heat of silver is 0.057 and this divided into 6.2 gives 109 as the approximate atomic weight of silver. But 215.76 grm. of silver will combine with 16 grm. of oxygen. Since 215.76 is so nearly twice 109, it is evident that in this case two atoms of silver combine with one of oxygen, and that the atomic weight of silver is $^{215.76}/_{2} = 107.88$. It cannot be too strongly emphasized that these atomic weights are ratio numbers, and that they or their integral multiples represent the proportions by weight in which the elements combine.

Symbols and Formulas.—In order to save time and also fo the sake of securing a convenient method for the representatio of the composition of substances, a system of symbols ha been devised which shall at the same time represent the elements and the atomic weights of the elements, and which by combining the symbols of the elements shall represent the compounds, the molecular weig [illegible] ounds and their composition. This system was devised [illegible] celebrated Swedish chemist Berzelius. The symbols for [illegible] elements are derived from the names of the elements, using [illegible]e Latin or Greek word where there is a difference in the nam[illegible] as we pass from language to language. In most cases the sy[illegible]bol is the first letter of the name, for example, the symbols of oxygen and hydrogen are O and H respectively. In case [illegible] the names of more than one element begin with the same letter, the symbol of the element is formed from this initial letter and a characteristic letter from the name. Take for example chlorine with the symbol Cl. The first letter of the symbol is *always* a capital and the *second* is *always* a small letter. In addition to representing the element one of these symbols also stands for an atomic weight of the element, and so represents a certain number of parts by weight of the element. O stands for oxygen, and 16 parts by weight of oxygen; H for hydrogen, and 1.008 parts by weight of hydrogen; Cl stands for chlorine, and 35.46 parts by weight of chlorine.

Hydrogen and chlorine combine to form hydrogen chloride in the proportion of 1.008 parts by weight of hydrogen to 35.46 parts by weight of chlorine, or of one atomic weight of the one element to one of the other. This is the composition of hydrogen chloride and both hydrogen chloride and its composition can be represented by writing the symbols of the elements close together, viz., HCl. This HCl stands first fo hydrogen chloride; second for a mole of hydrogen chloride, that is, 36.468 parts by weight of the substance; third it shows that a mole of hydrogen chloride is formed by the combination of one atomic weight of each of the elements, or of 1.008 parts b weight of hydrogen to 35.46 parts of chlorine. The sum of thes atomic weights gives the molecular weight or the parts by weigh of the hydrogen chloride represented by the formula HCl.

Water is formed by the union of 2.016 parts by weight o

MUTILATION NOTED JAN 26 1937

The formulas of the elements are obtained by applying the inciples in the section on Symbols and Formulas. An inspec- on of the third and fourth columns of the table shows that the toms of an element are usually not identical with its molecules, ut that one of the latter is generally made up by the union of wo or more atoms. For example, the molecule of oxygen con- ains two atoms of oxygen and has a formula of O_2. At first ight, it might appear that this is due to our choice of oxygen as the standard substance for both atomic and molecular weights, and arbitrarily giving it an atomic weight of 16 and a molecular weight of 32; and that if we had called it 16 in each case, that the atom and the molecule would have been identical. But the following reasoning will show that the atom cannot be the same as the molecule. Hydrogen and oxygen combine to form water in the proportion of two volumes of hydrogen to one of oxygen, (see p. 67) forming two volumes of water vapor. If we take as the unit of volume the volume of one gram mole—22,400 c.c. under standard conditions—we will have the following volume and weight relations:

2 × 22,400 c.c. of hydrogen + 22,400 c.c. oxygen = 2 × 22,400 c.c. water vapor.

2 × 2.016 grm. of hydrogen + 32 grm. oxygen = 2 × 18.016 grm. water vapor.

Then 2 grm. moles of hydrogen react with 1 grm. mole of oxygen to form 2 gram moles of water vapor; but each gram mole of a substance on the basis of Avogadro's hypothesis contains the same number of molecules. Therefore there are just twice as many molecules of water as there are molecules of oxygen. The assumed indivisibility of atoms makes it impossible to assume that a molecule of water contains less than one atom of oxygen; hence if a molecule of water contains one atom of oxygen, a molecule of oxygen must contain two atoms. Therefore if the atomic weight of oxygen is taken as 16, its molecular weight *must* be 32. This then is the basis for the apparently arbitrary choice of 32 as the molar weight of oxygen (p. 68).

Chemical Equations.—As was said above, two atomic weights of hydrogen unite with one of oxygen to form a mole of water; this can be very well shown with the aid of symbols as follows;

$$H_2 + O = H_2O$$

and this is an example of a chemical equation. A chemical equation is a very simple shorthand method of representing a chemical reaction quantitatively. For example, the above equation shows that 2.016 parts by weight of hydrogen will combine with 16 parts by weight of oxygen to form 18.016 parts by weight of water. The unit of weight may be the gram, pound or any other [illegible] and the equation will hold just the same.

We have learned [illegible] es of hydrogen will combine with one volume of o[illegible] two volumes of water vapor, or two moles of hyd[illegible] nole of oxygen will give two moles of water vapor [illegible] ing this we shall have to use the molecular form[illegible] thing. Now the molecular weights of hydrogen an[illegible] re twice their atomic weights so their molecular form[illegible] $_2$ and O_2 respectively. We may show that two moles of hydrogen combine with one of oxygen thus,

$$2H_2 + O_2 = 2H_2O$$

This is read "two moles of hydrogen combine with one mole of oxygen to give two moles of water vapor." The coefficients or numbers before the formulas show the number of moles taking part in the reaction, while the subscripts show the number of atomic weights of that element per mole. The coefficients therefore multiply every symbol in the formula which they stand before, as for example, $2H_2O$ represents 2 moles of water of 2 × 2 atomic weights of hydrogen and 2 × 1 atomic weights of oxygen. On either side of the above equation there are represented then, four atomic weights of hydrogen and two of oxygen. This is the proof that the equation is properly "balanced." There are two main principles involved in writing these equations. First, the formulas separated by + should be molecular formulas, and second, there must be the same number of atomic weights of any given element on either side of the equation, since otherwise we would be indicating a deviation from the la the conservation of weight. The advantage of writing mol formulas lies in the fact that since gram moles of gases oc equal volumes under like conditions we can tell at once t proportion by volume, from a simple inspection of the numbe ıoles of the one that reacts with the other. The proportions volume in which gases react are given by the coefficients in molecular equation for the reaction.

Vhen one of these equations is first worked out, it must be nd by experiment just what things are formed by the sub- ıces which react and the proportions by weight of everything olved in the process. There is no other way of doing it. We st know what is brought together and what is formed before can represent it by symbols. Students often think that they l to grasp the idea of equations because they cannot write wn symbols and formulas for a number of substances on one le of the equation and then tell by some rule what to put on e other, or else they jump to the other extreme and think that e symbols can be combined in any way at the fancy of the iter. But the truth of the matter is that only certain sub- ınces are formed from certain other ones, and one must know ıat these are and then represent them. Every equation then presents the results of actual experiment. It will be recalled at water and sodium react and form sodium hydroxide and ydrogen. The sodium hydroxide contains per mole 23 parts by eight of sodium, 16 of oxygen, and 1.008 of hydrogen. Its rmula then is NaOH and the molecular weight is a little over 0. We find by experiment that when 36.032 grm. of water act on 46 grm. of sodium that 2.016 grm. of hydrogen and 0.016 grm. of sodium hydroxide are formed. We may represent iis by the following equation,

$$2H_2O + 2Na = H_2 + 2NaOH$$

In studying the properties of substances it is very essential to arn with what other substances they will react and the sub- ances formed. It is not necessary to learn in what propor- ıns they react as, given the other information, the proportions n be reasoned out from the rules for balancing which were ven above.

Knowing the substances and their weights we can write the ıation, or given the equation we can work out the weights m the atomic weights.

CHAPTER VII

HYDROGEN PEROXIDE

Hydrogen and ox[illegible]ine in the ratio of one part by weight of hydrogen [illegible] by weight of oxygen, and in no other ratio whe[illegible] form water. However, they will combine in a [illegible] rtion for the formation of an entirely distinct su[illegible] as hydrogen peroxide. The ratio in this case is [illegible] ht of hydrogen to 15.886 parts by weight of oxygen. [illegible] compare the parts by weight of the oxygen in the two compounds which will combine with one part of hydrogen we see that they stand to each other as 1:2

$$7.943 : 15.886 = 1:2$$

This is the first time that we have found a really simple weight relationship and this you will notice is the ratio between the weights of the one element which will combine with unit weight of the other element in the two compounds. This sort of a simple weight relation has been found to be so common that a law has been formulated to describe it.

The Law of Multiple Proportions.—*If two elements, which we may represent by A and B, combine to form more than one compound then the number of grams of A which combine with one gram of B in the first compound will stand to the number of grams of A per gram of B in each of the other compounds in the proportions of whole numbers and usually these numbers are small ones.*

Hydrogen and oxygen always combine in one fixed ratio for the formation of water, and in another equally fixed for the formation of hydrogen peroxide, so the law of definite proportions describes the composition of each of these compounds and the law of multiple proportions applies to the two taken together.

Preparation and Properties of Hydrogen Peroxide.—Hydrogen peroxide is prepared in a number of ways, but the greater part of that used is made by the action of dilute sulfuric acid upon hydrated barium peroxide, barium sulfate being formed at the same time. It is not practical to prepare it directly from the elements although minute quantities are formed by allowing the flame of an oxy-hydrogen blowpipe to play upon ice. The hydrogen peroxide prepared by the interaction of barium peroxide and sulfuric acid is present in a dilute solution with water. To prepare pure hydrogen peroxide is not easy, but the method usually adopted depends upon the fact that hydrogen peroxide is less volatile than water, so that if a mixture of the two be distilled, relatively more of the water than of the hydrogen peroxide will pass off, and the residue will contain more and more hydrogen peroxide per cubic centimeter. By repeating the process, nearly pure hydrogen peroxide may be obtained. Hydrogen peroxide is rather unstable and decomposes into water and oxygen. This reaction like nearly all others goes more rapidly at high temperatures than at lower ones, therefore the process of distillation is carried out under diminished pressure because this lowers the boiling-point.

Hydrogen peroxide is a rather thick, syrupy liquid which has a very faint greenish-blue color somewhat more intense than that of water. Its density at 0°C. is 1.46. It melts at −2° and boils at 69° under a pressure of 2.6 cm. of mercury. Its boiling-point under atmospheric pressure is not known as it decomposes with explosion before it boils. It is odorless and has an astringent bitter taste. It is soluble in water in all proportions and the solution looks like water. This solution slowly decomposes into water and oxygen and keeps best in the dark, in a cool place, and when it contains a little acid. This transformation seems especially sensitive to the presence of foreign substances which after the completion of the process are found unchanged. These substances are therefore catalyzers. The following is a partial list of the catalyzers of the decomposition of hydrogen peroxide; charcoal, silver, gold, platinum, manganese dioxide, potassium and sodium hydroxides, saliva, and blood. The solid substances mentioned act the more vigorously the finer they are powdered.

A 3 per cent. solution is a standard article of commerce. It is often called a 10-volume solution from the fact that it will evolve, when all the hydrogen peroxide is decomposed, about ten times its volume of oxygen. This solution will rapidly destroy bacteria, and hence is much used as a disinfectant.

Oxidizing Action of Hydrogen Peroxide.—Since hydrogen p oxide gives up part of its oxygen so easily that it will do it ev at ordinary temperatures, it seems very natural to expect th it will be able to give it up to other things which can combine wi oxygen and thus oxidize them. Upon trial this is found to the case, and this action is exhibited more strongly as t hydrogen perox e concentrated; that is, th greater the weig e per cubic centimeter. If th pure hydrogen ght in contact with many in flammable subs. are oxidized so rapidly tha they ignite spon olutions are much less intens in their action activity as the dilution i increased.

Substances w oxygen to other substance in the way that hydrogen peroxide does are called oxidizin agents. As we shall see later, oxidizing agents can do man things besides give up oxygen to other substances, but this i one of the things which they may do, and must be kept in min until finally we come to a definition of an oxidizing agent whic will cover all cases. Other oxidizing agents are like hydroge peroxide, in that they act more vigorously as their concentratio increases. Because of its action as an oxidizing agent, hydroge peroxide is able to change many organic coloring matters int colorless substances, and it is therefore used for bleaching hai feathers, ivory, silk, wool, bones, leather, etc. For this purpo fairly dilute solutions are used.

Reducing Action of Hydrogen Peroxide.—When hydrog peroxide acts upon many oxides such as those of silver, go and mercury, the metals, water and oxygen are produced. T process of obtaining a metal from its oxide is an example reduction, and hence hydrogen peroxide acts in these cases a reducing agent. Potassium permanganate is also reduced hydrogen peroxide and in this case again oxygen is evolved.

Determination of the Molecular Weight of Hydrogen Peroxid—Hydrogen peroxide is so unstable that it is not possible determine its molecular weight from its gaseous density, but r course must be had to an entirely different method called t "Freezing-point Method."

It will be recalled that mention has been made of the f that any dissolved substance lowers the freezing-point of water, and also that gram moles of the various substances produce equal physical effects. Experiment has shown that if a gram mole of substance be dissolved in 1,000 grm. of water, the freezing-point of the water is lowered 1.85°C. This then furnishes a ready method for the determination of the molecular weight of such substances as hydrogen peroxide which cannot be vaporised without decomposition. The molecular weight of a substance, with some exceptions, as noted below, is identical with the number of grams of the substance required to lower the freezing-point of 1,000 grm. of water 1.85°C.

Any convenient weight of the solute and of water may be used and the molecular weight of the solute calculated from the equation,

$$M = 1{,}850\frac{w}{LW}$$

in which "M" represents the molecular weight of the solute, "w" the weight of the solute, "W" the weight of the water, "L" the lowering of the freezing-point.

The molecular weight of hydrogen peroxide determined in this way comes out close to 34.

Under the discussion of water it was pointed out that solutes lowered the vapor pressure of their solvents and that there was a connection between this fact and the fact that the solutions froze at lower and boiled at higher temperature than their pure solvents. From these facts, one would be led to expect that there would be a constant rise in the boiling-point of water per gram mole of solute per 1,000 grm. of water, because gram moles are in the main, physically equivalent. This is found to be the case. One gram mole of a substance with the exceptions noted below will raise the boiling-point of 1,000 grm. of water 0.52°C., and a method for the determination of molecular weights is based upon this. The formula is

$$M = \frac{520w}{rW}$$

in which M, w, and W have the same significance as before, and "r" is the rise in the boiling-point, and 520 the proportionality constant.

As has been implied above, there are some exceptions to the rule that a gram mole will lower the freezing-point of 1,000 grm. of water 1.85°C or raise the boiling point 0.52°C. We will find later that these exceptions lead to very interesting and important conclusions. All these exceptional substances yield solutions which are conductors of electricity. Hydrogen peroxide in solution is a non-conductor, so we may feel confident that the molecular weight given above is correct.

Composition and Formula of Hydrogen Peroxide.—Before the formula of any compound can be worked out the substance must be analyzed or synthesized and its molar weight determined. From the data the formula is then made up in a way which may be well illustrated by hydrogen peroxide.

The analysis of hydrogen peroxide shows that it consists of 5.93 per cent. hydrogen and 94.07 per cent. oxygen.

From these data and its molecular weight 34.016, it is a simple matter to calculate the number of parts by weight of each element per mole of the peroxide as follows:

$$\frac{34.016 \times 5.93}{100} = 2.016 \text{ parts by weight of hydrogen}$$

and

$$\frac{34.016 \times 94.07}{100} = 32.0 \text{ parts by weight of oxygen.}$$

Since the atomic weight of hydrogen is 1.008 and of oxygen is 16, it is evident at a glance that there is in a mole of hydrogen peroxide two atomic weights of hydrogen and two of oxygen and therefore its formula is H_2O_2.

Equation for the Preparation of Hydrogen Peroxide.—As has been already mentioned, hydrogen peroxide may be prepared by the action of dilute sulfuric acid upon barium peroxide, barium sulfate being formed at the same time. The equation for the reaction is as follows:

$$BaO_2 + H_2SO_4 = BaSO_4 + H_2O_2$$

in which BaO_2 stands for 169.37 parts by weight of barium peroxide, H_2SO_4 for 98.076 parts by weight of sulfuric acid, $BaSO_4$ for 233.43 parts by weight of barium sulfate, and H_2O_2 for 34.016 parts by weight of hydrogen peroxide.

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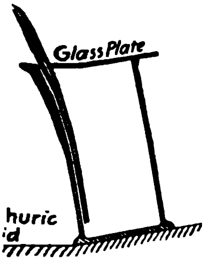

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evolved or absorbed, evolution being indicated by a plus (+) sign and absorption by a minus (−).

To illustrate this, let us consider the heat effect accompanying the burning of hydrogen to form water. For every gram mole of water produced 68,400 calories or 286 kilojoules of heat are evolved. This is represented as follows:

$2H_2 +$ [illegible] $+ 2 \times 68{,}400$ cal.

or $2H_2 +$ [illegible] $+ 2 \times 286$ Kj.

The heat effect acc[illegible] formation of a gram mole of a substance is called [illegible]ation, so the heat of formation of water is 286 K[illegible]. per mole.

There are two po[illegible]tion with thermochemical equations such as tho[illegible]which must be carefully kept in mind. The first one is—that if a certain quantity of heat is evolved during the formation of a gram mole of a substance, precisely the same quantity of heat will be taken up during its decomposition. The second is that the heat effect accompanying a given transformation depends only upon the initial and final states of the substances and not at all upon the intermediate stages through which they pass.

The Heat of Formation of Hydrogen Peroxide.—Since hydrogen and oxygen combine with such difficulty to produce hydrogen peroxide it is not possible to determine the heat of formation of this substance by direct measurement. This magnitude may, however, be calculated by taking advantage of the facts pointed out above. Hydrogen peroxide spontaneously decomposes into water and oxygen, and the heat effect belonging with this change may be easily measured. It is 97 Kj. or 23,100 cal. per mole of peroxide transformed. The equation is

$$2H_2O_2 = 2H_2O + O_2 + 2 \times 97 \text{ Kj.} \qquad \text{(I)}$$

From what has been said above and the law of the conservation of energy, it follows that if oxygen and water should unite to form hydrogen peroxide that 97 Kj. of heat would be absorbed for each gram mole of peroxide formed, the equation being

$$2H_2O + O_2 = 2H_2O_2 - 2 \times 97 \text{ Kj.} \qquad \text{(II)}$$

The heat of formation of the peroxide from oxygen and water therefore is − 97 Kj. To obtain the heat of formation from the elements, all that is necessary is to add to the above number the heat of formation of the water. In fact these thermochemical equations may be handled like ordinary algebraical equations. To equation (II) may be added the equation for the formation of water and the result will be the equation for the formation of the peroxide from its elements.

$$\begin{array}{l} 2H_2O + O_2 = 2H_2O_2 - 194 \text{ Kj.} \qquad \text{(II)} \\ \underline{2H_2 + O_2 = 2H_2O + 572 \text{ Kj.}} \\ 2H_2 + 2O_2 + 2H_2O = 2H_2O_2 + 2H_2O + 378 \text{ Kj.} \end{array}$$

or

$$2H_2 + 2O_2 = 2H_2O_2 + 2 \times 189 \text{ Kj.}$$

So the heat of formation of hydrogen peroxide is 189 Kj. or 45,300 cal. per gram mole. Of course the thermochemical equations expressed in cal. may be substituted for those in Kj. and the figure 45,300 will then be obtained directly.

The method applied here is a general one for calculating the heat effects which cannot be directly measured.

CHAPTER VIII

CHLORINE

The third [illegible] h we will discuss is chlorine. element does [illegible] e in nature but is found in ver quantities in [illegible] such as sodium, potassium, an nesium chlori [illegible] ent itself and many of its com are of very gr [illegible] not only in the chemical ind but also in [illegible] he sodium chloride, Na example, is [illegible] nd we all know how in sable this is. [illegible] ide is found in enormous qua in beds of rock salt at many places on the earth's surfa is present in still larger quantities in the ocean.

Chlorine was first prepared by Scheele in 1774, but that an element was first shown by Sir Humphrey Davy in 18

Preparation of the Element.—There are a few chloride as those of gold and platinum, which will decompose into c and the metals upon being raised to a high temperature, bu chlorides are so expensive and difficult to make that chlo practically never prepared in this way. The preparat chlorine, then, resembles that of hydrogen more nearly th of oxygen, in that a compound of chlorine is treated wit substance which will convert the rest of the chlorine com into a substance which will readily take on a different p state from that of the gaseous chlorine and hence m easily separated from this element. Chlorine may also b ated by electrolysis of solutions of soluble chlorides very as hydrogen and oxygen may be prepared. In the case electrolysis of the chlorides, chlorine is given off at one ele and either hydrogen or the metal of the chloride is depos the other.

The most suitable substance for the chemical prepara chlorine seems to be hydrochloric acid, a compound of c and hydrogen whose formula is HCl. From this hy chloride or hydrochloric acid, we can easily prepare chlor converting the hydrogen into water. This may be done in several ways. Gaseous hydrogen chloride mixed with oxygen or air may be passed through a tube containing clay balls or pieces of pumice stone coated with copper chloride or sulfate, heated to 370° to 400°C. Under these conditions water and chlorine are produced according to the equation,

$$4HCl + O_2 = 2H_2O + 2Cl_2$$

The copper salt acts as a catalyzer.

When air is used the product is of course greatly contaminated with nitrogen, as well as unchanged hydrogen chloride and oxygen, so that the method is not suitable for laboratory purposes, but was formerly largely used for the commercial preparation of chlorine, and is known as the Deacon Process.

Other Methods.—The preparation of chlorine from hydrogen chloride belongs to the processes which we call oxidation, and oxygen here is the oxidizing agent. Other oxidizing agents, if sufficiently powerful, may be used in the place of oxygen. Among those which are convenient may be mentioned manganese dioxide, MnO_2, potassium chlorate, $KClO_3$, potassium permanganate, $KMnO_4$, and bleaching powder, $CaCl_2O$. Each of these substances when treated with hydrochloric acid will oxidize the latter to water and chlorine.

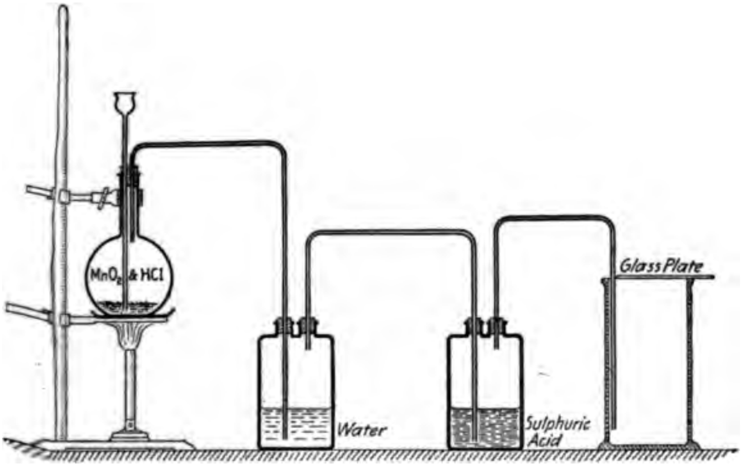

FIG. 19.

A very commonly used laboratory method for the preparation of chlorine is to gently heat a mixture of manganese dioxide with four times its weight of commercial hydrochloric acid (Fig. 19). The liquid first turns brown and then gives off greenish-yellow gaseous chlorine. After the reaction is finished, the solution contains manganous chloride, $MnCl_2$. The equation i

MnO_2 [illegible] $MnCl_2 + 2H_2O$

It seems to be ver[illegible] e reaction goes in two stages first forming wat[illegible] tetrachloride, $MnCl_4$, whic is dark colored, [illegible] trachloride decomposes int the lighter colored [illegible] de, $MnCl_2$, and chlorine, Cl_2 The equations rep[illegible] ıld be

M [illegible] $nCl_4 + 2H_2O$

and [illegible] $[nCl_2 + Cl_2$

Instead of starting with hydrochloric acid and manganese dioxide one may form the hydrochloric acid from salt and sulfuric acid and oxidize it with manganese dioxide right in th same vessel. To do this one warms a mixture of common sal and manganese dioxide with moderately dilute sulfuric acid The chlorine comes off very regularly, and at a convenient rate so that this modification of the first method is often used. Th equation is

$$2NaCl + MnO_2 + 3H_2SO_4 = MnSO_4 + 2NaHSO_4 + Cl_2 + 2H_2($$

Perhaps the most convenient laboratory method for the preparation of chlorine is to allow hydrochloric acid to fall drop b drop upon solid potassium permanganate, $KMnO_4$. The actio takes place promptly and at ordinary temperatures. Wate manganous chloride, potassium chloride, and chlorine are th products. The equation is

$$2KMnO_4 + 16HCl = 8H_2O + 2MnCl_2 + 2KCl + 5Cl_2$$

A very important method which is much used both in the laboratory and technically is to treat bleaching powder, $CaCl_2C$ with hydrochloric acid. Water, calcium chloride, $CaCl_2$, an chlorine are the products. The equation is

$$CaCl_2O + 2HCl = H_2O + CaCl_2 + Cl_2$$

It should be noted that in each of the above cases liquid water, non-volatile salt or salts, and gaseous chlorine are formed. This difference of state makes it easy to isolate the chlorine.

Technical Preparation.—Each of the above-mentioned methods for the preparation of chlorine, together with many others, has been used on a manufacturing scale, but at the present time the greater part of the chlorine of commerce is produced by the electrolysis of solutions of sodium or potassium chloride see Fig. 52, p. 281. The anode or positive electrode where the chlorine appears is usually made of graphite because almost everything else is attacked by the chlorine. At the cathode or negative electrode hydrogen is given off and sodium or potassium hydroxide is formed in solution. The process takes place as though metallic sodium or potassium were liberated at the cathode and then at once reacted with the water for the formation of hydrogen and sodium or potassium hydroxide.

Physical Properties.—At ordinary temperatures chlorine is a greenish-yellow gaseous substance whose density is 0.0032215 and whose uncorrected molecular weight is 72.13. Chlorine does not follow the gas laws very closely, a fact which is connected with the circumstance that it is very easily converted into a liquid either by cooling it to −33.6°C. under a pressure of one atmosphere, or by putting it under a pressure of 3.66 atmospheres at 0°C. or of 6.62 atmospheres at 20°C. The critical temperature is 146° and the critical pressure 94 atmospheres. After correcting for its deviations from the gas laws the molecular weight of chlorine is found to be 70.92.

Liquid chlorine has a greenish-yellow color, a density of 1.56, and is of an oily consistency. At −102° the liquid freezes to yellow crystals of solid chlorine.

Gaseous chlorine is soluble in about half its volume of cold water but is much less soluble in hot. Because of its solubility in cold water and the fact that it attacks mercury with great vigor, chlorine must be collected over hot water or by displacement of air. The latter is the more convenient, and since chlorine is nearly 2.5 times as heavy as air, it is easily carried out.

Chlorine has a very disagreeable odor, is exceedingly irritating to the mucous membrane of the throat and nose and has often produced death.

Chemical Properties.—The atomic weight of chlorine is 35.4 and its corrected molecular weight is twice this, so there are two atomic weights per mole and the formula is Cl_2. Chlorine is a rather more active element than oxygen and combines with almost all the other elements to form compounds called chlorides. In many cases the combination takes place with the production of light and heat, nbles the combustion of substances in oxygen, the resemblance that we call the phenomena c rine. In fact chlorine reacts so vigorously wit her substances that they will take fire spontan duced in the gas at ordinary temperatures. A ese be mentioned thin copper foil, phosphorus, and p an y. In each case a chloride is formed.

When completely dry, chlori much less active than when moist, and carefully dried liquid chlorine is now an article of commerce, being sold in strong steel cylinders lined with lead or bronze. One of the most important chemical properties of chlorine is that it is able to destroy many coloring substances, and it is therefore extensively used as a bleaching agent in the cotton and paper industries. It bleaches only in the presence of water, and is not able to destroy many of the minera dyes nor black tints due to carbon in the form of lamp black Chlorine makes all animal fibers very weak and therefore canno be used to bleach wool or silk.

It is a very powerful disinfectant and is much used to destroy bacteria.

Chlorine Water.—As has been mentioned, chlorine is fairly soluble in water. The solution, which has the greenish-yellow color, the odor, and taste, and bleaching qualities of the gas i called chlorine water. A portion of the gas undergoes a chemica change with the water, forming compounds which can best b discussed later. When exposed to sunlight, the chlorine disappears, oxygen is given off, and hydrochloric acid is left. Th equation is

$$2H_2O + 2Cl_2 = 4HCl + O_2$$

This reaction appears to be just the reverse of that takin place in the Deacon Process, but there is this difference that th eacon Process takes place in the gaseous state, while this es on in dilute solution; and under these circumstances the ydrochloric acid and oxygen are more stable than chlorine nd.water.

The action of chlorine upon water takes place slowly in the ark but much more rapidly in the light, and the more rapidly he stronger the light. The different kinds of light act quite ifferently; the red rays are almost without effect while the lue, violet and ultra-violet rays are especially active. This action of light is an example of what is known as photo-chemical action.

Chlorine Hydrate.—When chlorine is passed into ice-cold water, there soon separates out a greenish crystalline substance which is a compound of water and chlorine having the formula $Cl_2 \cdot 8H_2O$ and is called chlorine hydrate. It is a rather unstable compound breaking down at room temperature into chlorine and water.

Chlorine hydrate is now being prepared on a large scale as one of the steps in the process of manufacturing liquid chlorine from the impure gas obtained by the electrolysis of sodium or potassium chlorides The chlorine is cooled to a low temperature and exposed to the action of a spray of cold water. The hydrate is formed thus removing the greater part of the chlorine from the gaseous mixture. The hydrate decomposes at higher temperature into water and chlorine, the latter is dried and is then practically pure and ready for liquefaction.

The Naming of Chlorides.—As has been mentioned, the compounds of other elements with chlorine are usually called chlorides, prefixing the name of the other element to form the name of the compound, as for example—sodium chloride, potassium chloride, etc. If, as is not infrequently the case, the same element will form more than one compound with chlorine, it becomes necessary to distinguish between these substances. Where there are only two of these compounds, they are commonly distinguished by adding to the name of the element other than the chlorine the terminations -ous and -ic. The -ous being used for the compound containing the smaller and the -ic for that containing the larger amount of chlorine per combining weight of the other element. There are two chlorides of iron, the one $FeCl_2$ is called ferrous chloride, and the other $FeCl_3$ is called ferric chloride. Similarl we have mercurous chloride HgCl and mercuric chloride HgCl In some cases, particularly where there are more than tw compounds of an element with chlorine, the necessary distinctio is made by prefixing to the chloride the Greek word signifyin the number of combining weights of chlorine to a combinin weight of the other [illegible] example we have phosphoru trichloride, PCl_3 a [illegible] phor [illegible] entachloride, PCl_5. This sam system of nome [illegible] is [illegible] ed in distinguishing betwee the compounds in [illegible] ases [illegible] hich the same pair of element unite in different [illegible] ns [illegible] orm more than one compound For example, in t [illegible] of t [illegible] ides we have mercurous oxide Hg_2O; mercuric [illegible] rous oxide, FeO; ferric oxide Fe_2O_3; sulphur dioxide [illegible] $_2$ a [illegible] ulphur trioxide, SO_3.

Hydrogen Chloride.—Hydrogen chloride is an exceedingl important compound of chlorine. It may be formed by th direct combination of the two elements, which can be brough about in a number of ways most of which closely resemble thos which will induce the combination of hydrogen and oxyge For example, a stream of hydrogen will burn in an atmospher of chlorine much as in air except that the color of the flam will be a peculiar green instead of the blue of the ordinary flam A colorless gaseous compound is formed which fumes whe brought in contact with the air. This is hydrogen chlorid It is much more readily soluble in water than chlorine, does n bleach as chlorine does, but turns blue litmus red. Its solutio in water does not in any way resemble chlorine water, but highly acid and is identical with hydrochloric acid, of which w have had much to say. It has an odor which is disagreeable, b entirely different from that of chlorine. It has a very sour tast like all other acids, and in this respect also it differs material from chlorine. In fact hydrogen chloride is unlike chlorine color, odor, taste, solubility, action on colors, and in every oth property, both physical and chemical.

Another method for bringing about the combination of h drogen and chlorine is to mix the gases and pass an electric spa through a portion of the mixture. As was the case when this w done with a mixture of hydrogen and oxygen, the gases at on combine, with a violent explosion. If equal volumes of hydrog d chlorine are used, both of the gases entirely disappear, and e volume of the hydrogen chloride produced is equal to the um of the volumes of the separate gases. This shows that the ombination follows Gay Lussac's law of combining volumes. If n excess of either gas is used, that excess is left uncombined. The equation for the reaction is

$$H_2 + Cl_2 = 2HCl$$

which shows that one mole of hydrogen, 2.016 parts by weight of hydrogen, will combine with one mole of chlorine, 70.92 parts by weight of chlorine to form two moles of hydrogen chloride, or 2 × 36.468 parts by weight of hydrogen chloride. The composition of hydrogen chloride is 1.008 parts by weight of hydrogen to 35.46 parts by weight of chlorine, or 2.76 per cent. hydrogen and 97.24 per cent. chlorine.

If the mixed gases be heated to a temperature of between 240° and 270°C. explosion takes place. Hydrogen and oxygen, it will be recalled, behave in much the same way except that the combination takes place at a higher temperature.

There is one method for bringing about the combination of hydrogen and chlorine which entirely fails in the case of hydrogen and oxygen. This is with light. A mixture of hydrogen and chlorine combines very slowly in absolute darkness. If the mixture be exposed to light, the combination takes place at a rate which can be measured and which is proportional to the intensity of the light. In ordinary diffused daylight the reaction is complete in a few days, while if the mixture be exposed to full sunlight or to the light of burning magnesium, explosion almost instantly results.

Photochemical Action.—The action of light in accelerating the union of hydrogen and chlorine is another example of photochemical action. In this case the light certainly does not have to impart energy to the mixture, because the combination takes place even in the dark and always with a very great decrease in the energy so that a large amount of heat is evolved. A completely dry mixture of chlorine and hydrogen is insensitive to light, so water plays an important part in the process.

Action of Chlorine on Hydrogen Compounds.—Oxygen, it will be recalled, was able to act upon many compounds of hydrogen in

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such a way as to produce water. Similarly, chlorine will react with hydrogen compounds for the formation of hydrogen chloride. We have had an example of this in the case of chlorine and water. A still more striking case is that of chlorine and turpentine. Turpentine is a compound of hydrogen and carbon $C_{10}H_{16}$. If a piece of filter paper be dipped into some slightly warmed turpentine a[illegible]oduced into a cylinder of chlorine (Fig. 20, *a*), th[illegible]ter [illegible] combine with the hydrogen of the turpentine with [illegible] of so much heat that after a moment the turpent[illegible] a dark red flame which deposits all the carbon [illegible]f soot, and forms hydrogen chloride which may be [illegible]y its properties. Paraffine is composed of compounds [illegible]en and carbon, and when a burning paraffine candle ([illegible] is introduced into chlorine, it continues to burn, but wi[illegible]ned flame and the formation of hydrogen chloride and of soot, because under these circumstances chlorine does not combine with carbon.

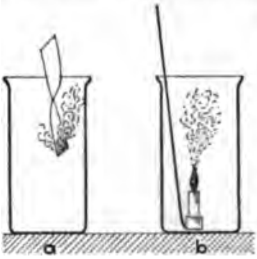

FIG. 20.

When natural gas is mixed with chlorine and exposed to sunlight, the methane, CH_4, which is the chief constituent of the gas, is attacked and hydrogen chloride, together with a number of chlorine substitution products of methane are formed. The first of these products is methyl chloride, CH_3Cl, and the final one is carbon tetrachloride, CCl_4. These actions take place slowly and at ordinary temperatures.

Laboratory and Technical Preparation of Hydrogen Chloride.—The methods previously given are not suitable for the preparation of any considerable quantity of hydrogen chloride. It therefore is almost invariably prepared by acting upon common salt—sodium chloride—with sulfuric acid. This action goes on in two stages. The first takes place at very moderate temperatures and consists in acting upon one mole of sodium chloride with one mole of sulfuric acid to form a mole of sodium acid sulfate and one of hydrogen chloride as shown in the equation

$$NaCl + H_2SO_4 = NaHSO_4 + HCl$$

At a considerably higher temperature the second stage takes lace and consists in acting upon a mole of sodium chloride with mole of sodium acid sulfate to form a mole of neutral sodium ulfate and one of hydrogen chloride,

$$NaCl + NaHSO_4 = Na_2SO_4 + HCl$$

These two equations may be added together to obtain one which will represent he complete process

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl$$

The operation is carried out in the laboratory in a glass flask, (Fig. 21) and the temperature cannot be raised high enough to carry it beyond the first stage. On a manufacturing scale the process is carried through the first stage in a large iron pan, A, heated from below (Fig. 22), covered with a brickwork dome; and finished in a fire clay muffle, B. Both dome and muffle are connected by a flue with brick towers filled with coke over which a small stream of water is kept trickling. The hydrochloric acid vapors pass up through the towers against the stream of water and are absorbed. Almost saturated hydrochloric acid runs out from the bottom of the first tower.

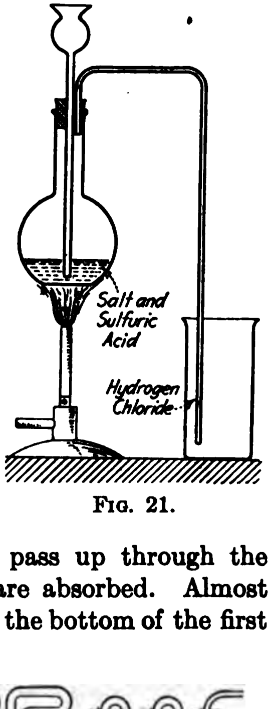

FIG. 21.

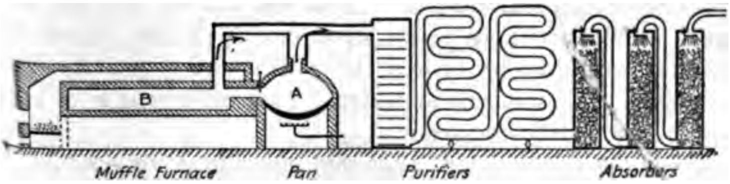

FIG. 22.

The reactions just given are reversible and would be incomplete were it not for the fact that the hydrogen chloride is very volatile and hence readily distilled from the mixture. This, of course, decreases the concentration of the hydrogen chloride, and more is at once formed to take its place. This will continue until the salt and sulfuric acid have been completely transformed, provid that the hydrogen chloride is carried off as it is formed.

The action takes place not because the hydrochloric acid i weaker acid than sulfuric acid—it is much stronger—but becau the hydrochloric acid is much more volatile than sulfuric ac In fact sulfuric acid may be replaced by any acid, however wea which is much less vo [illegible] ıydrochloric acid and which not a strong eno [illegible] nt to attack the latter. Ph phoric acid will [illegible]

First General [illegible] **Preparation of Acids.**—In t cases given abo [illegible] g with examples of a gene method for the [illegible] ion [illegible] acids from their salts. Tl may be called t [illegible] method for the preparation acids and may [illegible] ows. *Treat a salt of the ac desired with a less* [illegible] *distil. It is applicable to su acids as will stand distillation without decomposition, and course the added acid must not only be less volatile than the ac desired but must also be without action upon this acid.*

Properties of Hydrogen Chloride.—A number of properties hydrogen chloride have already been given; in addition we m state that its density is 0.00164 and molecular weight, 36.47. I critical temperature is 51.4°C. and its critical pressure 81.6 a mospheres. It can then be converted into a liquid by pressu alone at ordinary temperatures. At 22°C. the pressure nece sary is 46 atmospheres. The boiling-point of the liquid hydrog chloride is −83°C. and the freezing-point is −110°C. Tl liquid hydrogen chloride is a colorless almost inactive su stance which is without action upon metals or blue litmus, ai in general exhibits very little of the great chemical activity whi is shown by its solution in water. This difference is of gre import as we shall soon see.

As has been mentioned, hydrogen chloride is very soluble water. At its freezing-point one volume of water will abso about 525 volumes of hydrogen chloride. At the same time great amount of heat is developed which points to the formati of a compound with the water. This is indicated too by t fact that hydrogen chloride does not follow Henry's law of sol bility of gases which states that *provided no chemical reacti takes place between the gas and the solvent, the mass of the gas d* *solved by a given mass of the solvent is directly proportional to the pressure.* In the case of hydrogen chloride and water, Henry's law is far from describing the behavior. In fact the mass of the hydrogen chloride dissolved is but slightly altered by large changes in pressure. This would indicate that the hydrogen chloride undergoes some sort of a change upon passing into solution in water. As a matter of fact, by cooling very concentrated solutions of hydrogen chloride to low temperatures, three crystalline compounds of hydrogen chloride and water can be obtained. These are the mono-, di- and tri-hydrates, and have the formulas $HCl \cdot H_2O$, $HCl \cdot 2H_2O$, and $HCl \cdot 3H_2O$.

Constant Boiling Hydrochloric Acid.—Hydrogen chloride boils at −83°C. and water at 100°C. so one would naturally expect that a solution of hydrogen chloride would boil at temperatures between these two points. This is true, however, only of solutions containing more than 40 per cent. of hydrogen chloride. Weaker solutions boil at temperatures above 100°C. and a 20 per cent. solution boils at 110°C. and is the highest boiling and consequently the least volatile mixture of hydrogen chloride and water. If one distils a hydrochloric acid solution of less than 20 per cent. both water and hydrogen chloride come off, but relatively more of the former, and the residue becomes richer and richer in hydrogen chloride. After this process has gone on for some time, the residue finally reaches 20 per cent. hydrogen chloride which is the least volatile of the hydrogen chloride-

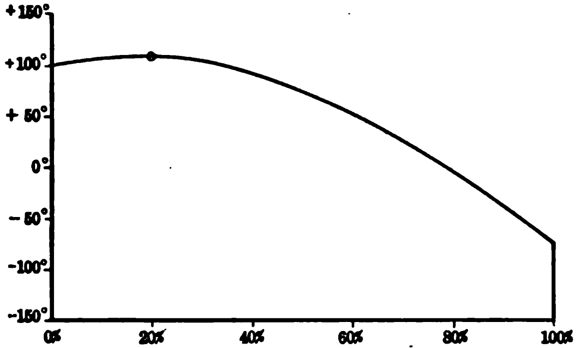

Fig. 23.

water mixtures, and boils at 110°C. After this has been reached, the mixture distils unchanged in composition and boiling-point.

If on the other hand we start to distil a hydrochloric acid solution containing more than 20 per cent. hydrogen chloride, this substance will come off with the water but in such quantities that the distillate contains a higher percentage of hydrogen chloride than the original mixture, leaving a residue which contains a smaller perc[illegible]gen chloride and boils at a higher and higher t[illegible]l its boiling-point becomes 110°C. and its con[illegible] cent. hydrogen chloride. After this it boils con[illegible]hanged composition. From the above it follows t[illegible]hat the original composition of the hydrochloric a[illegible]boiled for sufficient time the residue will be a 20 p[illegible]ling at 110°C.

The relationship b[illegible]osition and boiling-point for hydrochloric acid is shown in [illegible]

This constant boiling hydrochloric acid has often been mistaken for a chemical compound, but that this is not the case is shown by the fact that its composition changes with the pressure. When the boiling is carried out under a pressure of 2.5 atmospheres, the composition is 18 per cent. hydrogen chloride, while at 0.066 atmospheres it is 23 per cent. hydrogen chloride.

CHAPTER IX

IONIC THEORY

he Ionic Theory, or the Theory of Electrolytic Dissociation is often called, is one of the most important tools of modern mistry, and this chapter will be devoted to its development. should always be the case, the facts which it was devised to lain will be given first and should be fully appreciated by the dent, and then the theory learned not as a fact, but as a pos- e explanation for the facts.

cids.—Mention has been frequently made in what has gone ore of acids; hydrochloric, sulfuric and phosphoric acids typical examples of this very important class of compounds. e acids comprise a large group of substances of very different mpositions which have certain well marked properties in com- n. For example, they all contain hydrogen as one of their ential constituents, and when in solution they all taste sour, dden litmus, and evolve hydrogen gas when brought in contact th magnesium or zinc. All acids are hydrogen compounds, t many hydrogen compounds are not acids. Water, turpen- e, sugar, olive oil, and many other substances contain hydro- n but will not evolve hydrogen when brought in contact with gnesium or zinc at ordinary temperatures, neither do they ste sour, nor redden litmus, and so are not acids. The hydro- n, then, of acids must be in some kind of a special condition, fferent from that of the hydrogen of other compounds, and since is is the only constituent which acids have in common, as is own by the appended list of acids and their formulas, the com- on properties of acids must be ascribed to the hydrogen in this ecial condition.

SHORT LIST OF THE MORE COMMON ACIDS

Hydrochloric acid,	HCl	Nitric acid,	HNO_3
Hydrobromic acid,	HBr	Phosphoric acid,	H_3PO_4
Hydriodic acid,	HI	Oxalic acid,	$H_2C_2O_4$
Sulfuric acid,	H_2SO_4	Acetic acid,	$HC_2H_3O_2$

The acids show their peculiar properties only when dissolv in water and a few other solvents. When in a perfectly pu state or dissolved in most solvents, they are as indifferent as pu hydrogen chloride and neither redden litmus nor evolve hydrog with magnesium. Of course, their taste in the entire absen of water cannot be determined. The water has then som thing to do with the transformation of the hydrogen of the aci into its special s [illegible] ection it will be recalled th there is evidence [illegible] hloride undergoes a chemic change when it [illegible] n in water.

Bases.—Base [illegible] er large class of substances varied composit [illegible] ids, have, when dissolved water, certain [illegible] ion. Their solutions all ha a peculiar alkal [illegible] feeling, and turn red litm blue. As will b [illegible] rtial list of bases given belo they all contain hydrogen and oxygen in the proportion of o atomic weight of the one to an atomic weight of the oth We express this by saying that they contain the hydroxyl grou OH, and ascribe their common properties to this group.

List of Bases

Sodium hydroxide,	$NaOH$	Calcium hydroxide,	$Ca(OH$
Potassium hydroxide,	KOH	Barium hydroxide,	$Ba(OH$
Ammonium hydroxide,	NH_4OH	Strontium hydroxide,	$Sr(OH$

Like the acids, these bases show their common properties on when dissolved in water and a few other solvents, and since the are many compounds known which contain hydroxyl and y are not bases, we ascribe the characteristic properties of bas in water solution to the hydroxyl in a peculiar condition, simil to that of the hydrogen from acids in such solutions.

Neutralization.—When a solution of hydrochloric acid added to a solution of sodium hydroxide in just the proper pr portions, both the characteristic properties of the acid and th of the base completely disappear, and the solution which is l behind neither turns blue litmus red nor red litmus blue. It h neither a sour nor an alkaline taste, has no soapy feeling and d not evolve hydrogen at ordinary temperatures with zinc or ma nesium. Its taste is a pure salty one and in fact it is in eve way identical with a solution of common salt, sodium chlori in water. If the solution be evaporated, nothing but water passes off, and nothing but sodium chloride is left behind. What then has become of the hydroxyl of the base and the hydrogen of the acid? Obviously they must have combined to form water, leaving the sodium and chlorine to form sodium chloride.

The reaction may be represented by the equation

$$NaOH+HCl=H_2O+NaCl$$

We say that the hydrochloric acid and sodium hydroxide have neutralized each other and that water and a solution of sodium chloride have been formed. Other acids and bases behave in much the same way. They neutralize each other and leave solutions of the corresponding salts. For example, potassium hydroxide and nitric acid give water and a neutral solution of potassium nitrate, KNO_3

$$KOH+HNO_3=H_2O+KNO_3$$

Sulfuric acid gives sulfates and water

$$2NaOH+H_2SO_4=2H_2O+Na_2SO_4$$

Reacting Ratio in Neutralization.—By inspection of the above equations and writing others, it is very easy to satisfy one's self that a quantity of a base which contains 17.008 grm. of hydroxyl will just neutralize a quantity of an acid which contains 1.008 grm. of hydrogen in the peculiar acid condition. Since it is a very easy matter to tell with the aid of litmus just when a solution is neutral, the fact mentioned above is made the basis of a simple and much used method for the quantitative determination of acids and bases. The essentials of the method are as follows: Such a quantity of a base, say sodium hydroxide, as will contain 17.008 grm. of hydroxyl is dissolved in water and the solution made up to just a liter. Each cubic centimeter will then contain 0.017008 grm. of hydroxyl and will neutralize that quantity of an acid which will contain 0.001008 grm. of hydrogen, that is to say, 0.03647 grm. of hydrogen chloride for example. Such a solution is called a **normal solution** of a base. To use this in determining the amount of an acid, say hydrogen chloride, in a solution of unknown strength one would weigh out a few grams of the acid, add a drop of litmus soluti then run in from a graduated vessel called a burette (Fi enough of the normal hydroxide solution so that the lit just on the point of turning blue, and in fact is neith nor red. The number of cubic centimeters used multip 0.03647 gives the weight of hydrogen chloride in the acid s

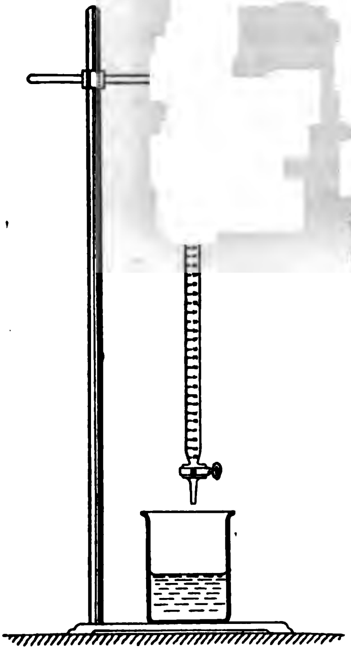
FIG. 24.

ken. Suppose that we w t 10 grm. of the acid an ired 20 c.c. of the normal utralize it. The acid co this 10 grm. is

20×0.03647 = 0.7294 or
per cent.

nilarly with the aid of a acid, *i.e.*, one containing 1.0 of hydrogen in the acid co per liter, one may determi easily the quantity of bas solution of unknown streng

Methods like the above very frequent use in quan chemical analysis, and are volumetric methods.

Acids, Bases, and Salt two Sets of Properties.— acid has when in solution in two independent sets of pro one common to all acids a dently belonging to the hy of the acid, and the other peculiar to that acid, being sh no other acid, and evidently belonging to the rest of t other than the hydrogen. For example, hydrochloric like all other acids in that it is sour, reddens litmus an hydrogen with zinc, but differs from all other acids i it will give sodium chloride with sodium hydroxide, a will yield a white curdy precipitate with silver nitrate precipitate is silver chloride. A few other acids give so similar precipitates with silver salts, but these all differ suff in their properties from the silver chloride so that they may be positively distinguished from the latter.

Bases too have two independent sets of properties in water solutions, the one common to all bases and evidently due to the hydroxyl, and the other peculiar to the particular base that is being worked with and belonging to the rest of the base other than the hydroxyl. For example, barium hydroxide shows all the characteristic properties of bases, turning litmus blue, etc., and also gives with sulfuric acid and all sulfates a white precipitate of barium sulfate, $BaSO_4$, which is different in its properties from all other substances. No other base has just this property. When one of these acids with its two sets of properties is neutralised by a base with its two sets, the properties common to all acids together with those common to all bases completely disappear leaving behind that set of properties of the acid which was peculiar to that particular acid, and the set of properties of the base which was peculiar to that base. So the salt solution remaining after the neutralization of an acid by a base has two sets of properties.

It follows from what has just been said that solutions of hydrochloric acid and all soluble salts of hydrochloric acid should give the white curdy precipitate of silver chloride upon the addition of silver nitrate. This is exactly what has been found to be the case. Similarly barium salts formed by the neutralization of this base by acids should and do give precipitates of barium sulfate upon the addition of sulfuric acid or sulfates.

When these same bases, acids and salts are in the pure state or even in solution in most solvents other than water, they do not exhibit these two sets of independent properties, but each has only one. An explanation for these and for the succeeding sets of facts will soon be given as the theory of electrolytic dissociation.

Abnormal Lowering of the Freezing-point.—In connection with the discussion of hydrogen peroxide it was brought out that a gram mole of a normal substance lowers the freezing-point of 1,000 grm. of water 1.85°C. and that this may be made the basis of a method for the determination of molecular weight. In fact we got the molecular weight of hydrogen peroxide in this way. The law of the molecular lowering of the freezing point is more exact for dilute solutions than for concentrated ones and we will

be more accurate if we state it as follows: A gram mole of
mal substance lowers the freezing point of 1000 kgrm. of
0.00185°C.

The acids, bases and salts are the exceptional subs
which do not lower the freezing-point of 1,000 kgrm. of
0.00185°C. per gram mole, but always produce a greater low
In many cases rly twice what we would e
in others som imes, and sometimes even
than three tin per gram mole dissolved in
kgrm. of water.

For example, h rogen de is a gaseous substanc
its molecular be d from its gaseous density
36.47. If on v m. of hydrogen chloride in
kgrm. of wat t of the water is lowered a
twice 0.00185 A gram m of sodium or potassium ch
or of any other salt formed by the union of one atomic w
of a metal with one atomic weight of chlorine produces abo
same lowering as a gram mole of hydrogen chloride whe
solved in 1,000 kgrm. of water or about twice 0.00185°.
salts as calcium or barium chloride, $CaCl_2$ or $BaCl_2$, whicl
tain two atomic weights of chlorine to one atomic weight
metal, lower the freezing-point nearly three times 0.0018
mole of salt in 1,000 kgrm. of water. From these facts it
as though the lowering for salts were 0.00185°C. per gram a
weight of each element instead of per gram mole. That
not the case is shown by the fact that nitric acid, HNO_3,
sium nitrate, KNO_3, and sodium nitrate, $NaNO_3$, only low
freezing-point of 1,000 kgrm. of water approximately
0.00185° per gram mole of acid or salt. In more concen
solutions these acids and salts give lowerings which are abn
but not as much so as in the dilute solutions; however, e
the most dilute solutions the abnormality is never greater
the figures just given. These facts are very significan
important in connection with the theory soon to be develo

Electrolytes.—Metals are called conductors of the first
As is well known, they are not altered in any way by the c
except that their temperature is more or less raised.
solutions are also conductors of electricity and are called
ductors of the second class because they are not only b

heated, but also are invariably decomposed during the passage of the current provided the circuit consists in part of conductors of the first class as is usually the case. Such solutions are called electrolytes and are formed only when acids, bases, and salts are dissolved in water or in the few other solvents in which they each show their two independent sets of properties. The decomposition takes place at points where the electric current enters and leaves the salt solution. The terminals of the metallic portion of the circuit are called electrodes and are distinguished from each other by calling that electrode where the electricity enters the solution the anode and that where it leaves it for the metal, the cathode. During the passage of the current, one kind of substance appears at the cathode and an entirely different substance at the anode. When hydrogen chloride solution is electrolyzed Fig. 25, hydrogen appears at the cathode and chlorine at the anode. The two substances appearing at the electrodes are in general the two substances which seem to give to the salt solutions their two sets of independent properties.

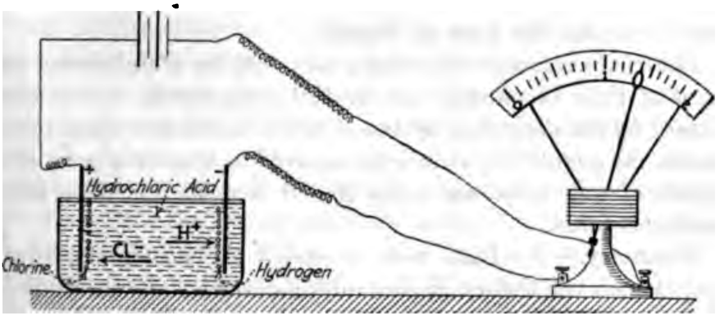

FIG. 25.

A fact which is closely connected with those given above, and which is still more significant is that, when a current of electricity is passed through a salt solution, the two components of the salt which act chemically independently of one another may actually be seen to move slowly in opposite directions, the one toward the cathode and the other toward the anode, and at quite different rates. Especial precautions must be taken to bring this out, but the experiments are rather easily performed and are quite definite in their results.

In the case of hydrochloric acid solutions, the chlorine moves toward the anode while the hydrogen travels toward the cathode, and moves nearly five times as rapidly as the chlorine.

The Law of Faraday.—The English scientist Faraday in the year 1833 carefully investigated the phenomena occurring at the electrodes and devised the names which we have been using such as electrolysis, electrolyte, electrode, anode, cathode, and in addition he called the substances which travel toward the electrodes ions. Those which move toward the cathode being the cations and those which move toward the anode being the anions. He also discovered facts which are described by the following law known as the Law of Faraday.

Electricity moves in electrolytes only with the simultaneous movement of their chemically independent components, and is accompanied by the deposition of two different substances upon the electrodes, the quantity of electricity required to liberate a gram atomic weight of any substance being 96,500 coulombs or some integral multiple of this.

Summary.—We have now discussed the principal groups of facts which the theory of electrolytic dissociation was devised to explain, but before proceeding to the theory itself a brief summary of these facts may be of use.

First.—Salts in solution in water showstwo independent sets of chemical properties; all salts having a common component have one set of properties in common. The term salt as used here includes acids and bases as well as salts in the ordinary sense.

Second.—Salts in solution in water lower the freezing-point of the water more than 0.00185°C. per gram mole per 1,000 kgm. of water; some nearly twice, some three times, and some even more than three times the normal lowering.

Third.—Salts in solution are electrolytes and the electricity passes through the solution only with the simultaneous movement of the components of the salts in opposite directions and at quite different rates. In addition two different substances are liberated at the electrodes. One gram atomic weight of each substance is liberated by the passage of 96,500 coulombs or some rational multiple of this.

All these are well established facts. The theory which is about to be given is simply an imagined cause or explanation for these and is in many respects on a par with the atomic theory. very useful in correlating a great many facts of chemistry ıas been very successful in predicting the discovery of new and hence is worthy of considerable attention.

e **Theory of Electrolytic Dissociation.**—To explain the facts ıed above, certain **assumptions** are made concerning the 'e of salts in solution. The first one is that when salts are .ved in water, they are immediately decomposed or dissociinto at least two different substances which are chemically ate and distinct from each other and from the original salt. ε new substances are assumed to be the chemically indeently acting components of the salts and are called **ions,** from Greek word *ιών* meaning wander, because they move in oppolirections toward the electrodes. That which goes toward node is known as the **anion** and that toward the cathode as **ation.**

ch gram mole of salt which dissociates is assumed to give o at least 2 gram moles of these new substances, the ions, each gram mole of an ion, or for brevity "gram ion," is ned to act in lowering the freezing-point of water like a gram of any other substance.

) account for the electrical properties of salt solutions, it is ned that these new substances, the ions, are charged with ricity, the cations with positive and the anions with negative ricity; the charges amounting to 96,500 coulombs or a gral multiple per gram ion. Since salt solutions are electricneutral, it must be assumed that the + charges upon the ns just equal the − charges upon the anions.

ıe **explanation** of the first group of facts, p. 108, by the theory ry simple. We have only to say that each of the two indeent sets of properties belongs to one of the new substances ns formed by the dissociation of the salt, and since these ions ssumed to be uncombined, each set of properties is of course endent of the other component of the salt. The chlorine ion umed to be identical whether it comes from hydrochloric HCl, sodium chloride, NaCl, potassium chloride, KCl, or other chloride, and hence all chlorides in solution show the erties of chlorine as ion no matter what the other ion may be. cid properties are ascribed to hydrogen as ion and since this

In terms of this theory a **salt** is any substance which whe dissolved in water yields ions.

An **acid** is a salt which when dissolved in water gives hydrogen as one of its ions.

A **base** is a salt which when dissolved in water gives hydroxyl as one of its ions.

Neutralization of Acids an[illegible].—When we come to consider the neutralization of acids a[illegible] in the light of the theory, we reach the rather surprising [illegible]ion that in the process only water is formed. The salt in [illegible] narrow sense, is not formed since its cation and anion exist[illegible]s such in the solution of the base and acid before they we[illegible]rought together and continue to do so after the process is fi[illegible]d.

To illustrate, let us give t[illegible]ations for a few reactions of this kind.

$$\begin{aligned}
Na^+ + OH^- + H^+ + Cl^- &= H_2O + Na^+ + Cl^-\\
K^+ + OH^- + H^+ + Cl^- &= H_2O + K^+ + Cl^-\\
Na^+ + OH^- + H^+ + NO_3^- &= H_2O + Na^+ + NO_3^-\\
K^+ + OH^- + H^+ + NO_3^- &= H_2O + K^+ + NO_3^-\\
2Na^+ + 2OH^- + 2H^+ + SO_4^{--} &= 2H_2O + 2Na^+ + SO_4^{--}\\
Ca^{++} + 2OH^- + 2H^+ + 2Cl^- &= 2H_2O + Ca^{++} + 2Cl^-
\end{aligned}$$

In every case water is formed and water only. The cation of the base and the anion of the acid are left unaltered. This explains why these salt solutions show the properties which were peculiar to the particular base and acid from which they were formed.

Heat of Neutralization.—Whenever any of the acids and bases given in the above list neutralize each other there is always 57 Kj. of heat evolved per mole of water produced, and this is true of all other strong acids and bases as well. This fact is very easy to explain on the basis of the electrolytic dissociation theory. In the light of this theory, water is the sole product of the actions and is always formed from the same substances, h as ion and hydroxyl as ion, and therefore each reaction show the same heat effect; and thus 57 Kj. or 13,600 cal. is t of formation of water from hydrogen and hydroxyl as i e salts had really been formed, the heat effect should have been fferent in each case.

Action of Acids.—In our previous discussion of acids, certain oints of similarity, their taste, action on litmus, metals, etc., ere made much of and ascribed to their common constituent ydrogen, in what we termed the ionic state. In other respects cids show great similarity. Quantities of different acids which ontain equal amounts of ionizable hydrogen are equivalent to ach other in several ways. They will, for example, neutralize the same quantity of any given base, say sodium hydroxide, and also when brought in contact with an excess of metal, like zinc, evolve equal quantities of hydrogen. Such quantities of acid as contain equal weights of ionizable hydrogen are appropriately called equivalent quantities, and that weight of any given acid which contains 1.008 grm. of ionizable hydrogen is called a gram equivalent of that acid. It will be recalled that a gram equivalent of an acid in 1,000 c.c. of solution is called a normal solution of the acid.

In some respects acids show striking points of dissimilarity. If pieces of zinc of equal area are introduced into equivalent solutions of hydrochloric, sulfuric, and acetic acids, hydrogen will be evolved in each case, but at very different rates in the different acids. If normal acids are used, less than 1 c.c. of hydrogen will be liberated from the acetic acid, and 65 c.c. from the sulfuric acid during the time required for the liberation of 100 c.c. from the hydrochloric acid. If equivalent quantities of the acids and an excess of zinc are used, ultimately, equal quantities of hydrogen will be liberated from each. In order to insure the success of the experiment indicated above, the pieces of zinc, before use should be treated with a dilute solution of copper sulfate. Copper will be deposited on the zinc and will tend to overcome the disturbing influence of local impurities in the zinc and secure a uniform evolution of hydrogen.

If we examine other cases in which these acids take part in reactions at measurable rates, we discover that their rates stand in the same order as in their action on zinc.

Much the same relationship exists between the lowering of the freezing-points of these acids. One gram mole of hydrochloric acid, it will be recalled, lowers the freezing-point of 1,000 grm.

of water nearly twice the normal lowering of 1.85° per mole; while a gram mole of acetic acid per 1,000 grm. of lowers it only a trifle more than 1.85°.

Normal solutions of these acids show very much these differences in their power to conduct electricity. The sol of hydrochloric acid is a good conductor; sulfuric acid somel like two-thirds [illegible] cetic acid, although still a ductor, is a poor [illegible]

Because of the [illegible] in their actions, everyone hydrochloric and [illegible] strong acids, and acetic a weak acid. The [illegible] id is considered to be some stronger than s [illegible]

Explanation.—It [illegible] ple matter to explain the outlined above [illegible] he ionic theory. We have to add to our [illegible] ious assum ions, that all acids break i ionize so as to give hydrogen as ion, and that this hydrogen a has the characteristic acid properties, the further assum that the various acids differ among themselves in the exte which they break up, or in their degree of ionization. H chloric acid is assumed to break up or ionize so far that in nc solution the greater part of the substance has been changed hydrogen and chlorine as ions, while under the same condi only a very small part of the acetic acid is supposed to be ion while sulfuric acid stands between the other two. Natural hydrogen as ion is the hydrogen which acts acid, that sol which contains the greatest concentration of hydrogen pr actually as ion will be the most intensely acid. This, from has been said, would be the hydrochloric acid, then would sulfuric and last the acetic far behind the other two.

We have learned that the rate at which any given subs will react, other things being equal, depends upon the co tration, and further that in terms of the ionic theory the rea between an acid and zinc is between hydrogen as ion and the From all that has been said above, then, it follows that th of evolution of hydrogen gas from these three acids should in the order, hydrochloric, sulfuric, and acetic acids. Thi the order found by experiment.

But if the acids differ so much in their degree of dissociati ionization, how does it happen that equivalent quantitie

:e the same amount of sodium hydroxide or any other
d also ultimately evolve the same quantity of hydrogen
ted upon by an excess of a metal? To explain this we
y to assume that the ionization of an acid is a reversible
and that as the hydrogen as ion is used up by combin-
ı hydroxyl or reacting with the metal, more of the
iated acid will break up into ions, and that this
will continue until the undissociated acid is completely

›tal acid hydrogen of an acid is called the ionizable hydro-
that fraction of it which is present at any one instant in
: of the free ion, is called the actual ion, while that which
ıociated, but capable of becoming ionized, is called the
l ion. The ionizable hydrogen is the sum of the actual
potential ions. Equivalent quantities of these three
ən contain the same amount of ionizable hydrogen, but
the relative proportions of the actual and potential
drogen chloride having the most actual and acetic the

ɛplanation of the difference in the lowering of the freezing-
so obvious that it need not be gone into here.

bility of a gram mole of an electrolyte to conduct elec-
s called its molecular conductivity. It may be de-
l by ascertaining the number of amperes of electricity
ill flow through a conductivity cell when the whole of
.tion containing a gram mole of the solute is placed
electrodes 1 cm. apart and a potential of 1 volt is

ule the molecular conductivity of a salt increases as the
of the solution in which one gram mole is dissolved is
d, *i.e.*, as the solution is diluted. With the great majority
:olytes, the molecular conductivity increases with the
up to a certain point, and then runs along without any
increase as far as the measurements can be carried—
words, it reaches a maximum.

;ural explanation for this is that the molecular con-
y of a solution is proportional to the fraction of the gram
ich is present as ions or the degree of ionization or disso-
ıs it is called and to the speed with which the ions move.

Assuming that the latter is constant as the solution is diluted, it follows that the degree of ionization of the electrolyte increases with the dilution, and that when the conductivity has reached its maximum, the salt is entirely ionized or completely dissociated. The degree of dissociation at any given dilution, can be found by dividing the molecular conductivity at that dilution by the maximum molecular conductivity at very great dilution. The results given in the follow table have been obtained in this way. Dilution as used here means the number of liters of the solution which contains one g m mole of the acid. It will be seen from this table that even moderate dilutions, the first three acids are almost complet dissociated and are about as strong as possible. The sulfuri cid is distinctly weaker, but quickly gains in strength. The drofluoric and acetic acids are much weaker, but grow rapidly stronger. So the more dilute the acids the stronger they become in the sense that they are more largely dissociated. ***That acid is the strongest which is most easily broken up into its ions.*** No adequate reason has been offered as to why hydrochloric acid is so highly and acetic acid so slightly dissociated.

Dilution	HCl	HBr	HI	HF	H_2SO_4[1]	$HC_2H_3O_2$
1	0.784	....	....	0.07	0.51	0.004
10	0.95	0.95	0.95	0.10	0.57	0.013
100	0.98	0.98	0.98	0.26	0.79	0.050
1,000	0.99	0.99	0.99	0.95	0.93	0.125

Bases, like acids, differ widely in the degree of their dissociation at moderate dilutions. Sodium and potassium hydroxides being highly dissociated. Calcium and barium hydroxides have about the same degree of dissociation as sulfuric acid at any given dilution, while ammonium hydroxide is weak like acetic acid.

Salts, in the common sense of the term, are with few exceptions highly dissociated, and that too whether they are salts of weak or of strong acids. Sodium acetate, for example, at any given dilution is only a little less dissociated than sodium chloride.

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[1] The sulfuric acid solutions are equivalent and not molecular solutions.

ydrogen Ion as An Oxidizing Agent.—When an acid acts upon a l and hydrogen is given off, the reaction seems to be between hydrogen ion and the metal. For example, the equations

$$Zn + 2H^+ + 2Cl^- = Zn^{++} + 2Cl^- + H_2$$
$$Zn + 2H^+ + SO_4^{--} = Zn^{++} + SO_4^{--} + H_2$$

cate that neither the chlorine nor the sulfate ion is changed, le the zinc is transformed from the metal to the ion and the rogen from the ion to the free element. This change of the from the metal to the ion is considered oxidation and the drogen ion is the oxidizing agent. This type of oxidation must kept in mind until a full definition of oxidation and reduction be offered.

CHAPTER X

OXY[illegible] S OF CHLORINE

General.—Neith[illegible] hlorine nor oxygen, hydroge and chlorine coml [illegible] by more or less roundabou methods three oxid [illegible] s containing oxygen, oxyacid as they are called, [illegible] d. The following table giv the names and form [illegible] ds, the sodium salts of the acids, and the oxides.

Acids		Salts	
HCl	Hydrochloric acid	$NaCl$	Sodium chloride
$HClO$	Hypochlorous acid	$NaClO$	Sodium hypochlo
$HClO_2$	Chlorous acid	$NaClO_2$	Sodium chlorite
$HClO_3$	Chloric acid	$NaClO_3$	Sodium chlorate
$HClO_4$	Perchloric acid	$NaClO_4$	Sodium perchlor

Oxides

Cl_2O, Chlorine monoxide or hypochlorous anhydride.
ClO_2, Chlorine dioxide or chlorine peroxide.
Cl_2O_7, Chlorine heptoxide or perchloric anhydride.

These oxyacids and their salts furnish excellent illustrations the law of multiple proportions.

Nomenclature of Acids and Salts.—The names of aci formed by the union of hydrogen with one other element an which consequently do not contain oxygen are formed by takin the characteristic part of the name of the element other tha hydrogen and adding the prefix hydro- and the suffix -ic. F example hydro-chlor-ic acid. Salts of such acids are named b combining the name of the metal which replaces the hydroge of the acid with another word formed by dropping the prefi hydro- from the name of the acid and replacing the -ic by -id For example, sodium chloride.

In naming the oxyacids the best known is usually designate by adding to the characteristic part of the name of the elemen ther than hydrogen and oxygen the suffix -ic. For example, ClO_3 is called chloric acid. The names of the salts of such acids nd in -ate, as sodium chlorate, $NaClO_3$.

If there is an acid containing more oxygen than the -ic acid, it is distinguished by adding to the name of the -ic acid the prefix per- and similarly for the salt as perchloric acid, $HClO_4$, and sodium perchlorate. That acid containing the next smaller amount of oxygen than the -ic acid is distinguished by the suffix -ous and its salts are called the -ites. For example, chlorous acid, $HClO_2$, and sodium chlorite.

If there is an acid containing a still smaller amount of oxygen than the -ous acid, it is distinguished by adding to the name of the -ous acid the prefix hypo- and its salts are called hypo- . . . . -ites; for example, hypochlorous acid and sodium hypochlorite.

The Preparation of the Oxygen Compounds of Chlorine.—The first step in the preparation of the oxygen compounds of chlorine is the reaction between water and chlorine.

$$H_2O + Cl_2 \rightleftarrows HCl + HClO$$

From the hypochlorous acid so formed, hypochlorites can be prepared by neutralization with bases. From these hypochlorites by appropriate means chlorates, perchlorates, chlorites, and the oxides of chlorine may be made. The reaction between chlorine and water is therefore an important one and may appropriately be called the key reaction for the oxygen compounds of chlorine. It is reversible and is very incomplete under ordinary circumstances. Equilibrium results in this and other reversible reactions when the conditions described in what is known as the Law of Mass Action are fulfilled. In order that we may have a proper mastery of these reversible reactions, this law will now be developed.

The Law of Mass Action.—The law of mass action in the form in which it is to be developed here, applies to reversible reactions in equilibrium at constant temperature. Let us take a general case and say that we have a reversible reaction between A and B for the formation of C and D. Let a, b, c, and d represent the concentrations of A, B, C, and D respectively, and let R stand for the rate at which A and B combine for the formation of C and D, and R′ for that at which C and D react for the re-formation of A and B,

$$\begin{matrix} A + B \rightleftarrows C + D \\ a \quad\; b \quad\; c \quad\; d \end{matrix}$$

Then from what we have already learned, p. 44, the rate at which A and B react, everything else being constant, is proportional to a, and likewise to b, and therefore is proportional to their product since a number proportional to each of two or more numbers is proportional to their product or

$$R = Ka$$
$$R = K'b$$
$$R = K''ab$$

Correspondingly R′ the rate at which C and D react is proportional to the concentration of C and to that of D and hence to the product of these concentrations

$$R' = K'''c$$
$$R' = K''''d$$
$$R' = K'''''cd$$

Equilibrium will result in all such reactions when the two rates are equal, and therefore at equilibrium

$$R = R'$$

Hence

$$K''ab = K'''''cd$$

or

$$\frac{K''}{K'''''} = \frac{cd}{ab} = k$$

Expressed in words this would be: The product of the concentration of the resulting substances divided by the product of the concentration of the reacting substances is a constant for a reversible reaction in equilibrium at constant temperature. From this it follows that if the three substances A, B, and C react to form D, E, and F, equilibrium will result when def/abc reaches a certain definite constant value whose magnitude depends upon the nature of the substances and the temperature, but not upon the particular values of the concentrations which happen to exist in any one case. What is called the mass law equation for this reaction is:

$$\frac{def}{abc} = K$$

Suppose now that A is identical with B, then "a" will be identical with "b." The chemical equation then becomes

$$\begin{array}{c} A + A + C \rightleftarrows D + E + F \\ a \quad a \quad c \quad d \quad e \quad f \end{array}$$

or

$$2A + C \rightleftarrows D + E + F$$

and the mass law equation,

$$\frac{def}{aac} = \frac{def}{a^2c} = K$$

If A is identical with B and C and if D and E are identical, these equations become,

$$A + A + A \rightleftarrows D + D + F$$

$$3A \rightleftarrows 2D + F$$

$$\frac{ddf}{aaa} = \frac{d^2f}{a^3} = K$$

This may be expressed in words as follows: *When equilibrium results in a reversible reaction at constant temperature, the product of the concentration of the resulting substances divided by the product of the concentrations of the reacting substances—each concentration raised to that power whose exponent is the coefficient of the substance in the chemical equation—is a constant.* The content of this statement is the *Law of Mass Action.*

For an example of its application we may take the equilibrium between water vapor, iron, iron oxide, and hydrogen. The equation is

$$\begin{array}{c} 3Fe + 4H_2O \rightleftarrows Fe_3O_4 + 4H_2 \\ a \qquad b \qquad\qquad c \qquad\quad d \end{array}$$

The mass law equation is

$$\frac{cd^4}{a^3b^4} = K$$

Since solids and liquids change their volume so slightly with changes of pressure, it follows that the ratio of their mass to their volume is practically constant; therefore the concentration of a solid substance or of a homogeneous liquid is constant and only gases and dissolved substances have variable concentrations.

The iron and the iron oxide are solids so their concentrations are constant and may be combined with the equilibrium constant K. The conditions of equilibrium are therefore dependent upon the concentratio gen and of the water vapor. The mass law equatio s

$$\frac{d^4}{b^4} = \qquad = k$$

or

$$\frac{d}{b} =$$

This then tells us that the nces will be in equilibrium when there is a certain definite ratio between the concentrations of the hydrogen and of the water vapor.

It is very easy to see from this that if the concentration of the hydrogen be decreased, the water must react with the iron for the formation of more hydrogen and iron oxide. In a current of steam which sweeps away the hydrogen, equilibrium will never be reached and the reaction will continue until all the iron is used up.

The law of mass action is exceedingly useful in that it enables one to tell just what to do to make a reversible reaction run in either direction as desired, and further, if we know the magnitude of k, the value of the concentration of one substance can be calculated—given that of the others.

In accordance with the law of mobile equilibrium (page 57), chemical equilibrium is shifted in such a way that more and more of the substances, which are formed with the absorption of heat, will be present as the temperature rises.

From this it may be seen that K, the equilibrium constant, varies with the temperature. At any one temperature it is, however, independent of the absolute value of the concentrations.

Let us apply this mass law to the reaction between water and chlorine writing the latter ionically,

$$\begin{array}{ccccc} H_2O + & Cl_2 \rightleftarrows & 2H^+ + & Cl^- + & ClO^- \\ a & b & c & d & e \end{array}$$

his a, b, etc., represent the concentrations of the substances above them. Equilibrium will result when c^2de/ab has hed a certain definite ratio or

$$\frac{c^2de}{ab} = K$$

m this it may be easily seen that a decrease in the concentra- of one of the substances on the right hand of the equation decrease the numerator of the constant valued fraction, and must result in the reaction proceeding from left to right, ording to the above equation, until the values of a and b have n decreased and those of c, d and e have been increased suffi- ntly to restore the original equilibrium value for the fraction. the addition of any hydroxide, say sodium hydroxide, the con- tration of the hydrogen as ion, "c," may be decreased through formation of water, and practically all the free chlorine y be consumed. Carbonates, say sodium carbonate Na_2CO_3, anything else which will use up the hydrogen ion will act in same way. The carbonates use up the hydrogen ion through formation of carbonic acid, H_2CO_3, which is not much more oken up into its ions than water. The H_2CO_3 is unstable and aks down into water and gaseous carbon dioxide which escapes m the liquid in bubbles. The equations are

$$H^+ + Cl^- + ClO^- + 2Na^+ + 2OH^- = 2H_2O + 2Na^+ + Cl^- + ClO^-$$

d

$$H^+ + Cl^- + ClO^- + 2Na^+ + CO_3^{--} = H_2CO_3 + 2Na^+ + Cl^- + ClO^-$$

$$H_2CO_3 = H_2O + CO_2$$

e equations written in the ordinary way become

$$HCl + HClO + 2NaOH = 2H_2O + NaCl + NaClO$$

d

$$HCl + HClO + Na_2CO_3 = H_2O + NaCl + NaClO + CO_2$$

either case we say that sodium chloride and sodium hypo- lorite are formed. The reaction is not usually carried out by urating water with chlorine and then adding sodium hydroxide, OH, but by running chlorine into sodium hydroxide solution d the equation is often written,

$$2NaOH + Cl_2 = NaCl + NaClO + H_2O$$

but the action doubtless takes place in the stages indicated above. Other hypochlorites can be made from the hydroxides of the corresponding metals in much the same way by the direct action of chlorine upon the hydroxide, either in solution or in the solid state.

Without question the most important hypochlorite is that of calcium, which in the form of aching powder, or "chloride of lime," as it is often called, is manufactured by the thousands of tons from chlorine and calci hydroxide. This bleaching powder is not a pure hypochl e, but is a mixed salt, half chloride and half hypochlorite, rmed by the union of one atomic weight of calcium with an atomic weight of chlorine ion and one of hypochlorite ion. The formula of the salt is given in various ways. Perhaps the most common of these are

$$CaCl(ClO),\ Ca\begin{matrix}\diagup Cl\\ \diagdown ClO\end{matrix},\ \text{or}\ CaCl_2O$$

The equation for its formation is as follows,

$$Ca(OH)_2 + Cl_2 = CaCl(ClO) + H_2O$$

This bleaching powder is a solid and may be conveniently shipped. It is easily converted into chlorine, into sodium hypochlorite and chloride solution, or into hypochlorous acid. Upon passing into solution in water it acts as though it breaks up into calcium as ion and chlorine and hypochlorite ions.

$$CaCl(ClO) \rightleftarrows Ca^{++} + Cl^- + ClO^-$$

Upon the addition of sodium carbonate the very slightly soluble calcium carbonate, $CaCO_3$, is precipitated, and sodium, chlorine, and hypochlorite ions are left in solution.

$$Ca^{++}+Cl^-+ClO^-+2Na^++CO_3^{--} \rightleftarrows CaCO_3+2Na^++Cl^-+ClO^-$$

or

$$CaCl(ClO) + Na_2CO_3 \rightleftarrows CaCO_3 + NaCl + NaClO$$

The solution, containing sodium hypochlorite, obtained in this way is very largely used for bleaching cotton and linen goods in the laundries.

Solutions containing hypochlorite are often formed by elecrolysis of solutions of chlorides. Chlorine is liberated at the anode and hydrogen with the simultaneous formation of hydroxide at the cathode. The apparatus is so designed that the chlorine and hydroxide mix almost as soon as formed and hence hypochlorite is produced.

The hypochlorites either alone or when mixed with chlorides are good oxidizing and bleaching agents and also are excellent disinfectants. One very important use for bleaching powder is in the purification of water. This depends upon the fact that very small quantities of the substance will kill typhoid and other pathogenic bacteria without injuring the water for domestic purposes.

The ion ClO^- differs markedly in properties from the Cl^-. It is for example, a strong oxidizing agent and does not give a precipitate of silver chloride upon the addition of silver nitrate.

Decomposition of Hypochlorites.—Hypochlorous acid and its salts are unstable and readily undergo change. Sodium hypochlorite, for example, slowly decomposes into the chloride and oxygen:

$$2NaClO = 2NaCl + O_2$$

The addition of a small quantity of a cobalt salt results in the formation of a black precipitate of cobaltic hydroxide which acts as a vigorous catalyzer for the decomposition of the hypochlorites. In this way oxygen may be easily obtained from bleaching powder. By adding some cobalt salt to sodium hydroxide solution and then passing in chlorine, a steady stream of oxygen may be obtained. This reaction may be represented as follows:

$$4NaOH + 2Cl_2 = 4NaCl + 2H_2O + O_2$$

Mixtures of iron and copper sulfates work in practically the same way as cobalt salts and are used in the technical preparation of oxygen from bleaching powder.

This same decomposition of hypochlorites may be accelerated by light and takes place fairly rapidly in sunlight. The action of light on chlorine water finds an explanation from this fact. The chlorine acts on water, forming hypochlorous and hydrochloric acids, and the hypochlorous acid then decomposes into oxygen and hydrochloric acid:

$$H_2O + Cl_2 \rightleftarrows HCl + HClO$$
$$2HClO = 2HCl + O_2$$

or combining,

$$2H_2O + 2C \quad HCl + O_2$$

This ability of hypochlorous nd its salts to yield oxygen is closely connected with the ox power of these compounds.

In addition to decomposing xygen and chlorides, hypochlorites change slowly into ch es and chlorides. For example, sodium hypochlorite pass into sodium chlorate and chloride, as shown in the followi uation:

$$3NaClO = Na \quad + 2NaCl$$

This change takes place more rapidly when the solution is heated and especially if the solution is acid or contains an excess of chlorine. An alkaline solution of a hypochlorite is fairly stable.

The chlorate formed as described above slowly changes into chloride and perchlorate and the latter in turn decomposes into chloride and oxygen. In order that the reactions shall take place at a reasonable rate the temperature must be far above the boiling-point of water, so to obtain them the dry salts are heated. The equations are

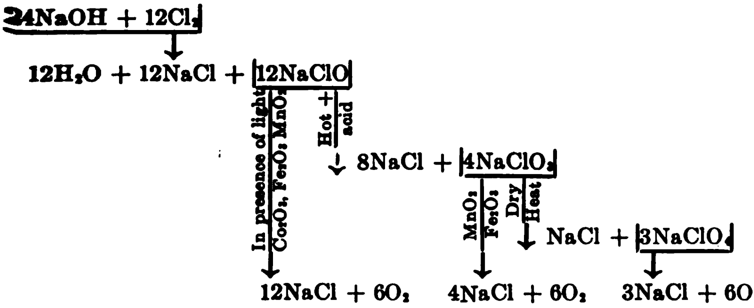
$$4NaClO_3 = 3NaClO_4 + NaCl$$

and

$$NaClO_4 = NaCl + 2O_2$$

The final result is that, after going through these stages, the hypochlorite ultimately is changed completely into chloride and oxygen as is the case with the cold solution in the presence of a cobalt salt. The hypochlorite, chlorate, and perchlorate are unstable substances, while the chloride and oxygen are stable. Except in the presence of cobalt oxide, etc., the system sodium hydroxide and chlorine does not pass directly to its most stab state, sodium chloride, oxygen and water, but goes through series of stages each more stable than its predecessor until t final stable condition is reached. In this respect, this syste seems to be typical of many others which behave similarily. So generally is this the case that it is described in what is called Ostwald's *Law of Successive Reactions,* which states that *a system does not pass directly from the least stable to the most stable state, but does so through a series of steps or stages of gradually increasing stability.*

We may represent the successive steps in the transformation of the unstable system, sodium hydroxide and chlorine, into the stable one, sodium chloride, oxygen and water as follows:



The conditions stated along each arrow show the factors which favor the change indicated by the arrow.

This is typical of the changes undergone by other systems of bases and chlorine and gives briefly a general scheme for the preparation of hypochlorites, chlorates, and perchlorates.

Hypochlorous Acid.—Hypochlorous acid is very volatile and will stand distillation, consequently it is easily prepared from its salts by the first general method, by adding to a hypochlorite a less volatile acid and distilling. The reaction must be carried out in rather dilute solution since the concentrated acid readily decomposes into water and chlorine monoxide, Cl_2O. Since hypochlorites are difficult to prepare pure, a mixture of hypochlorite and chloride is generally used. Hypochlorous acid $HClO$, is a very much weaker acid than hydrochloric, HCl and is almost exclusively formed if a little less acid is added than the amount required to act upon the hypochlorite which is present. It is very important that an excess of acid be avoided since hydrochloric and hypochlorous acids react very rapidly to form chlorine and water.

$$HCl + HClO = H_2O + Cl_2$$

Bleaching powder is usually used to furnish the hypochlorit and nitric acid is the added acid, care being taken to add it little at a time and to stir vigorously to avoid any local exces The equation is

$$2CaCl(ClO) + 2HNO_3 = 2HClO + CaCl_2 + Ca(NO_3)_2$$

Instead of nitric acid one n [illegible] se hydrochloric or still bette the very weak boric acid.

The hypochlorous acid form[illegible] is volatile and passes over wi the first part of the water. It [illegible]y be still further concentrat by fractional distillation.

Properties of Hypochlorous [illegible]**d.**—The anhydrous acid cann be prepared, so it is known [illegible] in solution. Its concentrat solutions have a yellow color [illegible] smell something like bleachi powder. In dilute solutions it is almost colorless. It neutrali strong bases and forms hypochlorites.

It is unstable and decomposes in several ways. When warme or exposed to sunlight, it may decompose into hydrochloric ac and oxygen.

$$2HClO = 2HCl + O_2$$

or it may change into hydrochloric and chloric acids.

$$3HClO = 2HCl + HClO_3$$

This latter change takes place even in the dark.

In the two cases given above, hypochlorous acid acts like oth hypochlorites, but hypochlorous acid differs in one respect fr other hypochlorites, and that is, in very concentrated solution will decompose into water and chlorine monoxide.

$$2HClO \rightleftarrows H_2O + Cl_2O$$

This reaction is reversible and hypochlorous acid is formed the union of water and chlorine monoxide; consequently t latter is often called hypochlorous anhydride. An **anhydr** is an oxide which will combine with water to form an acid.

As has been mentioned, hypochlorous acid is a powe oxidizing and bleaching agent, being more active in this resp than other hypochlorites. In fact, there is some little evide that solutions of hypochlorites owe a part of their bleaching po to the presence in them of hypochlorous acid. Hypochlorous acid bleaches because it oxidizes and destroys the coloring matters which are usually very complex carbon compounds. Each of these compounds owes its color to a certain definite combination of its constituents, and when this combination is broken up by oxidation or otherwise the color is destroyed. Usually the reaction is too complex to be represented by an equation.

It will be recalled that chlorine was not active as a bleaching agent until the article to be acted upon was moistened. It is probable that it is really the hypochlorous acid formed by the action of the chlorine on the water which does the bleaching. Cotton or linen goods are prepared for bleaching by boiling them in a soap solution for a time to remove grease and oils and then passing them through a dilute solution of bleaching powder and into very dilute sulfuric acid. The last two processes are repeated until the desired results are reached. The goods are then carefully washed to remove the excess of chemicals. The solutions must be very dilute and the operation carried out with care or a large part of the strength of the fabric will be destroyed. Even under the best conditions the cloth is considerably weakened. Wool, silk, and feathers are so greatly altered by chlorine, hypochlorous acid and hypochlorites, that they cannot be bleached by these substances. Hypochlorous acid is formed by the action of carbon dioxide, CO_2, upon moist bleaching powder,

$$2CaCl(ClO) + H_2O + CO_2 = CaCO_3 + CaCl_2 + 2HClO$$

and sometimes in bleaching, the goods which have been wet in bleaching powder solution, are simply hung in the air instead of being treated with sulphuric acid. Hypochlorous acid is a powerful disinfectant.

Chlorine Monoxide.—Chlorine monoxide or hypochlorous anhydride is usually prepared not by the decomposition of hypochlorous acid which was mentioned above, but by the action of chlorine on mercuric oxide whereby mercuric oxychloride and the chlorine monoxide are formed according to the following equation:

$$2HgO + 2Cl_2 = Cl_2O + HgOHgCl_2$$

The chlorine monoxide is a yellowish-brown gaseous substance which may be condensed to a liquid boiling at + 5°C. Its odor

easily forme
of hypochlorites as has been described
take place most readily when the soluti
and slightly acid or contain an excess of cl

Potassium chlorate is the most widely u
these salts, although sodium chlorate is
many purposes because the latter is more s

Potassium chlorate may be prepared by
chlorine into a warm concentrated solution
ide. The reaction takes place in stages as
sodium chlorate, the hypochlorite being
equations are

$$2KOH + Cl_2 = KCl + KClO$$
$$3KClO = 2KCl + KClO$$

or combining into one and omitting the inte

$$6KOH + 3Cl_2 = 5KCl + KClO_3$$

The chlorate is much less soluble than the
centrating the solution and allowing it to
separates out mixed with only a little of the
be removed by a second crystallization. As
equation just given, only one-sixth of the s
potassium hydroxide is converted into chlo
formed at the same time, occurs in nature in
has a comparatively small value. On a manu
waste is avoided by first

This reaction is reversible and far from complete, but the potassium chlorate is only moderately soluble in cold water, while the potassium chloride is easily and the calcium chloride and chlorate exceedingly soluble; so when the solution is concentrated and cooled, potassium chlorate passes out of solution in the form of crystals. As the potassium chlorate separates from the solution more is formed until finally the greater part of the chlorate has been obtained in the form of the potassium salt.

Chlorates are also very largely made by electrolysis, the process being very much like that for the preparation of hypochlorites, the main difference being that the solution is kept hot and very slightly acid, conditions which it will be recalled are favorable to the change of hypochlorites into chlorates.

Properties of Chlorates.—All chlorates are at least moderately soluble in water, and many are so very soluble that they are deliquescent. Potassium chlorate is one of the least soluble of these salts, 100 parts of water at 0°C. dissolve 3.14 parts of this salt. The solubility increases rapidly with rising temperature so that at 100°C. it is approximately eighteen times that at 0°C.

The chlorates all give off oxygen upon being heated and are strong oxidizing agents. Because of this property they are much used in making fireworks, dyes, matches, and explosives. An intimate mixture of sugar, $C_{12}H_{22}O_{11}$, and potassium chlorate is sometimes used as a blasting powder, but like practically all other explosives containing chlorates, it is treacherous and dangerous to handle. The addition of a little castor oil makes these explosives safer.

Potassium chlorate, it will be recalled, was used in the laboratory preparation of oxygen. The equation is,

$$2KClO_3 = 2KCl + 3O_2$$

The oxygen so prepared almost always contains a trace of chlorine.

Like sodium chlorate, potassium chlorate if slowly and carefully heated will pass into potassium perchlorate, $KClO_4$:

$$4KClO_3 = KCl + 3KClO_4$$

Although chlorates are good oxidizing agents, they are less powerful than the hypochlorites being more stable compounds.

Preparation of Chloric Acid.—Chloric acid cannot be without decomposition and therefore cannot be prepar its salts by the first general method for the preparation c It is made by what is known as the second general method preparation of acids from their salts which is briefly as *Add to a solution of a salt of the desired acid another acid so chosen that the anion of the added acid shall form a ve cultly soluble compound with the cation of the salt.* Th pound is at once formed and passes out of solution, leav hydrogen ion of the added acid and the anion of the salt tion, that is, forming a solution of the desired acid. By evaporation, this acid may be then obtained in a pure or a more or less concentrated form. Of course the salt to and the acid to be added must be very carefully chosen, a the correct amount of each used. Silver chloride and sulfate are among the least soluble of the salts, so silver c $AgClO_3$, with hydrochloric acid, or barium chlorate, Ba(with sulfuric acid are well adapted for the formation of acid according to the following equations:

$$AgClO_3 + HCl = HClO_3 + AgCl$$

and

$$Ba(ClO_3)_2 + H_2SO_4 = 2HClO_3 + BaSO_4$$

Barium chlorate is much cheaper than silver chlorate, latter reaction is the one usually used. The acid solu filtered from the white precipitate of barium sulfate, BaS concentrated by evaporation at a temperature below until it contains 40 per cent. of the acid. The dilute sol colorless while the concentrated has a yellowish tint. strong acid.

The solution slowly decomposes in a number of ways. form perchloric acid, $HClO_4$,

$$4HClO_3 = HCl + 3HClO_4$$

or break down into hydrochloric acid and oxygen,

$$2HClO_3 = 2HCl + 3O_2$$

The HCl so formed then reacts with more $HClO_3$ to form c and water,

$$5HCl + HClO_3 = 3H_2O + 3Cl_2$$

addition it may go over into water, chlorine dioxide, ClO_2, and ygen.

$$4HClO_3 = 2H_2O + 4ClO_2 + O_2$$

When concentrated sulfuric acid is poured on a chlorate, chloric cid is formed, which at once decomposes as shown above. The hlorine dioxide so produced generally explodes spontaneously ith such violence that only very small quantities of chlorate hould be used.

Chloric acid has found no important application, but its salts are largely used.

Separation of Salts.—A solid salt generally separates from its solutions in the form of crystals, and the process of obtaining these is called crystallization. It is very evident from what has been learned, p. 61, that crystals cannot form in an unsaturated solution. In fact the solution must be more than saturated, supersaturated, before they can separate. But in the absence of the solid solute a solution may be considerably supersaturated without crystallization taking place.

Since most substances are more soluble at high temperatures than at low, it is usually very easy to prepare supersaturated solutions by making a saturated solution at a somewhat elevated temperature and then cooling the liquid after the removal of any excess of the undissolved solid. The cooled solution becomes supersaturated and may often be preserved for a long time in this condition by carefully excluding dust which usually contains enough small particles of the solute to bring about crystallization. Generally, however, it will spontaneously deposit crystals as soon as it reaches a certain degree of supersaturation. After the separation has once started it will continue until only so much of the solute remains dissolved as corresponds to its solubility at that temperature. If the supersaturated solution was prepared from crystals of the substance, the process of reobtaining the crystals is known as recrystallization, and is very commonly used in the purification of substances. The process of recrystallization which has just been outlined is especially adapted to the purification of such substances as change their solubility very rapidly with the temperature. Potassium chlorate is a good example. The process is not so well adapted to potassium chlor impure as before.

When a mixture of salts is dissolved in w
value of the solubility of each salt is more or
general relationships are left unchanged.
salt can crystallize, the solution must bec
with that particular salt. As a general rule

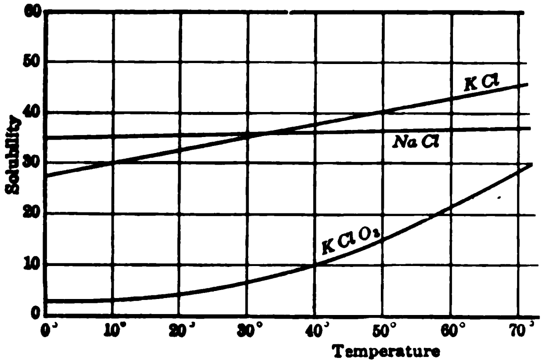


Fig. 26.

crystallize by itself, and if two or more sepa
time, a mixture of crystals of the salts will b
than crystals, each of which contains every sal

Upon the evaporation of a solution of a mi
say for example

It is not necessarily the least soluble salt which separates first, t that one whose point of saturation is first exceeded. This ay easily be the case with the more soluble salt if it is present relatively large quantities.

Perchlorates.—Potassium perchlorate is easily prepared by eating potassium chlorate until it melts and then keeping it at is temperature for some time. A little oxygen is given off and lids begin to form in the molten salt. After a time the hole thing goes solid, although the temperature has not been wered. The solid so formed is a mixture of potassium chloride, Cl, and potassium perchlorate, $KClO_4$. It is formed according the following equation,

$$4KClO_3 = 3KClO_4 + KCl$$

he evolution of the oxygen had nothing essentially to do with is reaction, and hence is not shown in the equation. It is rmed by the side reaction,

$$2KClO_3 = 2KCl + 3O_2$$

The potassium perchlorate, $KClO_4$, is only slightly soluble, so is easily separated from the potassium chloride, KCl, by finely wdering the mixture and dissolving out the potassium chloride th cold water. A recrystallization of the residue from hot ter yields pure potassium perchlorate, $KClO_4$.

The perchlorates are much more stable than the hypochlorites chlorates. Upon being heated they yield oxygen and chlorides, d may also act as oxidizing agents but are not as active as pochlorites or chlorates. They are all more or less soluble in ter, the potassium salt being one of the least soluble. Some them are used in matches and fireworks because they are safer an the chlorates.

Perchloric Acid.—Perchloric acid is easily formed from the tassium salt by the first general method, using sulfuric acid d cautiously distilling under diminished pressure. Dense ite fumes are evolved and a colorless or slightly yellow liquid tills, consisting of pure perchloric acid, $HClO_4$, which condenses the receiver.

Mixtures of perchloric acid and water act like mixtures of drochloric acid and water in that there is a const mixture of minimum vapor pressure and maximum boiling-poin This mixture contains 72 per cent. of acid and boils at 203°C By adding to this constant boiling mixture twice its volume concentrated sulfuric acid, and distilling, pure perchloric ac may be obtained.

The pure acid is volatile, boiling at 19°C. under a pressure 1.1 cm. of mercury; and has a density of 1.78. It is a goo oxidizing agent and decomposes with great readiness so th when brought in contact with oxidizable substances it general explodes with violence. When heated under atmospheric pre sure it decomposes at 92°C. It dissolves in water with a hissi noise and the evolution of much heat. The aqueous acid of a strengths up to the constant boiling mixture is entirely stabl Unlike hypochlorous and chloric acids, it does not liberat chlorine from hydrochloric acid. It combines with water t form white crystals of perchloric acid monohydrate $HClO_4{\cdot}H_2O$

Perchloric Anhydride.—Perchloric anhydride, Cl_2O_7, may b prepared by adding to perchloric acid phosphorus pentoxide P_2O_5, keeping the whole cool by a freezing mixture of ice an salt. After standing for a day the mixture is distilled. Th anhydride is colorless and boils at 82°C. It may be distille under ordinary pressure without danger, but explodes whe struck or brought in contact with a flame.

Chlorine Dioxide and Chlorites.—As has already been men tioned, one of the ways in which chloric acid decomposes, is int water, chlorine dioxide, ClO_2, and oxygen:

$$4HClO_3 = 2H_2O + 4ClO_2 + O_2$$

Chlorine dioxide is a yellow-brown gaseous substance whic may be condensed in a tube cooled with ice and salt. The boi ing-point of the liquid is about 10°C. Both the liquid and it vapor are extremely explosive. The vapor explodes whe brought in contact with a metal rod heated to a temperatu far below redness. The products of the explosion are chlori and oxygen.

When passed into sodium hydroxide solution, it yields a mixtu of sodium chlorate and chlorite, $NaClO_2$.

$$2NaOH + 2ClO_2 = NaClO_3 + NaClO_2 + H_2O$$

The chlorites are all unstable substances for which no applications have been found. The acid is known only in dilute solutions. The chlorites appear to stand between the hypochlorites and the chlorates in the order of stability, but the evidence is not entirely conclusive.

Relative Oxidizing Power.—It might very reasonably be thought that perchloric acids and chloric acids would be stronger oxidizing agents than hypochlorous acid, because the former contain more oxygen per mole; but this is not the case. Hypochlorous acid is the strongest, and perchloric the weakest. This is connected with the fact that hypochlorous acid is the most unstable and perchloric the most stable of the series.

CHAPTER XI

BROMINE, IODI[illegible]D FLUORINE

General.—Fluorine, chlorine, [illegible]ine and iodine form a group or family of elements which clos[illegible]semble one another in their chemical properties and those of [illegible]ompounds which they form. This group is called the haloge[illegible]y. From what is to follow, it will be seen that there is a reg[illegible] change in properties of the halogens and their compounds [illegible] the atomic weight of the element increases. It will also [illegible]ery evident that chlorine, bromine and iodine resemble each other much more closely than they do fluorine. For this reason the discussion of chlorine will be followed immediately by that of bromine and iodine and fluorine will be taken up last.

Bromine and iodine are so much like chlorine that a very fair knowledge of their chemistry may be easily obtained by comparison with that of chlorine, noting the many points of resemblance and the few differences. *The root of most of these differences lies in the fact that bromine is liberated from its compounds by weaker oxidizing agents than chlorine, and that iodine is still more readily set free than bromine.*

Bromine

Occurrence.—Like chlorine, bromine is never found free, but only in combination, chiefly as bromides of sodium, potassium, and magnesium. It is not nearly as abundant as chlorine, and its compounds are never found in anything like a pure state, but are always mixed with very much larger quantities of chlorides. It is found in sea water, many mineral springs, salt wells, and beds of rock salt. These beds of rock salt have doubtless been formed by the evaporation of sea water, so the presence of bromides in them is not surprising. The bromine content of salt beds differs rather widely, and naturally only the richer deposits are utilized as sources of bromine. The chief bromine-producing localities are Stassfurt in Germany, and Michigan, Pennsylvania, and West Virginia, in the United States.

Preparation of the Element.—From the fact that bromine is more easily liberated than chlorine, it follows that any of the oxidizing agents used in the preparation of chlorine may be employed for bromine, so we may match each of the methods given in the preceding chapter for the preparation of chlorine by a similar one for bromine, as shown by the following equations:

$$\begin{aligned}
4HCl + O_2 &= 2H_2O + 2Cl_2 \\
4HBr + O_2 &= 2H_2O + 2Br_2 \\
4HCl + MnO_2 &= MnCl_2 + Cl_2 + 2H_2O \\
4HBr + MnO_2 &= MnBr_2 + Br_2 + 2H_2O \\
2NaCl + MnO_2 + 3H_2SO_4 &= MnSO_4 + 2NaHSO_4 + Cl_2 + 2H_2O \\
2NaBr + MnO_2 + 3H_2SO_4 &= MnSO_4 + 2NaHSO_4 + Br_2 + 2H_2O \\
2KMnO_4 + 16HCl &= 2MnCl_2 + 2KCl + 5Cl_2 + 8H_2O \\
2KMnO_4 + 16HBr &= 2MnBr_2 + 2KBr + 5Br_2 + 8H_2O \\
CaCl_2O + 2HCl &= CaCl_2 + Cl_2 + H_2O \\
CaCl_2O + 2HBr &= CaCl_2 + Br_2 + H_2O
\end{aligned}$$

Electrolysis of chlorides and bromides yields respectively chlorine and bromine at the anode.

Of these reactions, that between the bromides, manganese dioxide and sulfuric acid (Fig. 27), is the most important because the bromides are much cheaper and more easily obtained than hydrobromic acid.

In addition to the above, bromine is liberated by a number of oxidizing agents which cannot act on chlorides. The element chlorine is an oxidizing agent, not as powerful of course as the ones used to set it free, but still powerful enough to liberate bromine as shown in the following equation:

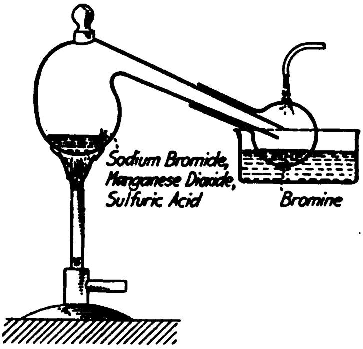


FIG. 27.

$$2NaBr + Cl_2 = 2NaCl + Br_2$$

The reaction is really between the free chlorine and the bromine ion:

$$2Br^- + Cl_2 = 2Cl^- + Br_2$$

and consequently is an exchange of charges, and yet the liberation of bromine from a bromide is considered oxidation; so this kind of exchange of charges must be counted oxidation and kept in mind until a general defini[illegible]dation and reduction can be given. It is by this reaction [illegible]ost of the bromine of commerce is obtained.

Concentrated sulfuric acid [illegible]irly strong oxidizing agent, strong enough to act on hy[illegible]ic acid, but not on hydrochloric acid.

$$2HBr + H_2SO_4 = [illegible] + SO_2 + 2H_2O$$

This last action must be kept [illegible]ind in the preparation of hydrobromic acid.

Physical Properties of Bromine.—Bromine is a dark, brownish-red liquid, which is almost opaque in thick layers, and has a density of 3.19. It boils at 59°C. and freezes at -7.3°C. The liquid produces very severe "burns" if it comes in contact with the skin. Bromine is an easily volatile liquid since its vapor pressure at ordinary temperature is about 20 cm. The vapor has a deep red color, an exceedingly stifling odor, and is very irritating to the mucous membrane. The name bromine is derived from the Greek word, *βρωμος*, meaning a stench. The density of the bromine vapors is five times that of oxygen and indicates a molecular weight of 160. Since the atomic weight of bromine (79.92) is half the molecular weight, its formula is Br_2. At higher temperatures the molecular weight becomes somewhat less, indicating a partial dissociation of the Br_2 into Br. Iodine shows this tendency still more strongly.

Bromine dissolves in water to the extent of about 3 parts by weight of bromine to 100 parts of water at ordinary temperature. The solution has a yellowish-red color, smells of bromine, and may often be used in the place of the latter when water does not interfere with the reactions. The solubility of bromine is markedly increased if the water also contains some soluble bromides. It is more soluble in carbon disulfide, alcohol, and many organic solvents than it is in water.

Chemical Properties.—The chemical properties of bromine are very much like those of chlorine, modified by the fact that it is slower and less intense in its action than the latter. It is a powerful oxidizing agent, though less so than chlorine. It combines directly with hydrogen and most of the other elements forming bromides. With water it forms a hydrate, $Br_2 \cdot 8H_2O$, which, in general, is similar to chlorine hydrate.

Hydrogen Bromide.—With slight modifications due to the facts mentioned above, that bromine does not combine as vigorously with hydrogen as chlorine does, and that hydrogen bromide is more easily oxidized than hydrogen chloride, practically every method given in Chapter VIII for the preparation of hydrogen chloride may be matched by a corresponding one for hydrogen bromide. This is shown by the following equations.

$$H_2 + Cl_2 = 2HCl$$
$$H_2 + Br_2 = 2HBr$$

The mixture of hydrogen and bromine does not explode when exposed to sunlight or an electric spark, as that of hydrogen and chlorine does, but combines fairly rapidly at high temperatures under the influence of platinum as a catalyzer.

$$NaCl + H_2SO_4 = HCl + NaHSO_4$$
$$NaBr + H_2SO_4 = HBr + NaHSO_4$$

In this case dilute sulfuric acid must be used in the preparation of hydrogen bromide because the concentrated acid is a strong enough oxidizing agent to liberate the bromine.

The indirect preparation of hydrogen bromide by the action of bromine upon compounds of hydrogen and carbon corresponds closely to that of hydrogen chloride by the action of chlorine upon these same compounds. For example, bromine and benzene, C_6H_6, react for the formation of hydrogen bromide and monobrombenzene, C_6H_5Br.

$$Br_2 + C_6H_6 = HBr + C_6H_5Br$$

The method which is generally the most convenient for the preparation of hydrogen bromide is by the interaction, at ordinary temperatures, of bromine, red phosphorus and water (Fig. 28). The action takes place in steps. First the bromine and the phosphorus combine for the formation of phosphorus tribromide, PBr_3.

$$2P + 3Br_2 = 2PBr_3$$

This then reacts with water to form phosphorous acid, H_3PO_3, and hydrogen bromide, HBr.

$$PBr_3 + 3H_2O = 3HBr + H_3PO_3$$

Hydrogen chloride might be [illegible]red in an analogous way, but the action is very violent and [illegible] method is not so cheap and convenient as that from salt and [illegible]lfuric acid.

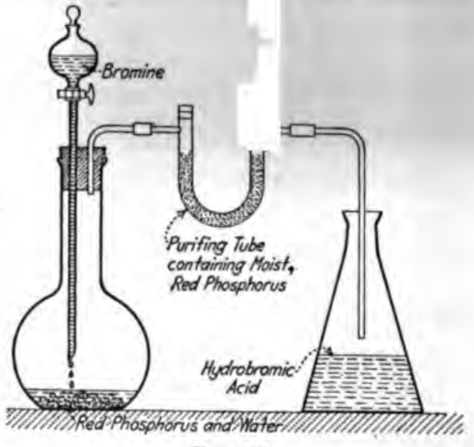


FIG. 28.

Properties of Hydrogen Bromide.—Like hydrogen chloride, hydrogen bromide is a colorless gaseous substance at ordinary temperatures. Its critical temperature is 91°C. At low temperatures it condenses to a colorless liquid, boiling at − 68.5°C. and freezing at − 86°C. The gaseous density of hydrogen bromide shows that it has a molar weight of 81, and the formula HBr. It is very soluble in water, 600 volumes of hydrogen bromide to one of water, and fumes upon contact with moist air. Like hydrogen chloride, it forms a maximum boiling solution with water. The composition of this is 48 per cent. hydrogen bromide, and it boils at 126°C.

Like hydrogen chloride, dry hydrogen bromide is a rather indifferent substance, but when in solution in water it is as ghly acid as hydrochloric acid and its solution is known as drobromic acid. It acts upon metals much as other acids do, rming hydrogen gas and solutions of the bromides of the metals. peaking in terms of the ionic theory, solutions of hydrobromic cid and bromides contain the bromine, ion Br^-. The properties f this ion are very much like those of the chlorine ion. It is olorless, forms a very difficultly soluble compound with silver, lver bromide, $AgBr$, which is less soluble than silver chloride nd has a slight yellow color. The liberation of bromine from he bromine ion by chlorine is the easiest way to distinguish he bromine ion from the chlorine ion. The equation for the eaction is

$$2H^+ + 2Br^- + Cl_2 = 2H^+ + 2Cl^- + Br_2$$

The free bromine colors the solution yellowish-red. If the solution be shaken with a little carbon bisulfide, the latter takes up most of the bromine from the water and becomes highly colored. This makes a very delicate test for bromine.

Oxygen Compounds of Bromine.—No one has, so far, succeeded in preparing oxides of bromine, perbromic acid, or perbromates, but hypobromous acid, $HBrO$, and bromic acid, $HBrO_3$, and their salts are well known. The reactions for their preparation are exactly analogous to those for the corresponding chlorine compounds. The first step is the reversible reaction between bromine and water for the formation of hydrobromic and hypobromous acids,

$$Br_2 + H_2O \rightleftarrows HBr + HBrO$$

When equilibrium results, the concentrations of the acids are even less than in the corresponding reaction for chlorine. The addition of sodium or potassium hydroxides will destroy the equilibrium by neutralizing the acids and cause the reaction to run toward the right until nearly all the bromine has been used up, and there results a solution of a mixture of the bromide and hypobromite salts.

$$HBr + HBrO + 2NaOH = NaBr + NaBrO + 2H_2O$$

or, combining the two equations

$$Br_2 + 2NaOH = NaBr + NaBrO + H_2O$$

The change of the hypobromites into bromates takes place even more rapidly upon heating, than the corresponding change of the hypochlorites. The equation is

$$3NaBrO = 2NaBr + NaBrO_3$$

Hypobromous acid is so unstable that even a dilute solution of it is hard to make and soon decomposes. Bromic acid may be made from its salts by the sec[illegible]neral method for the preparation of acids, or by the action [illegible]ochlorous acid upon bromine water:

$10HClO + Br_2 =$ [illegible] $+ 2HBrO_3 + 4H_2O$

[illegible]

Iodine occurs in natu[illegible] exclusively in combination, chiefly as iodides and i[illegible]s. [illegible]has, however, been found free in waters of certain mineral springs, having been liberated from hydriodic acid by the action of dissolved oxygen. This is in line with the fact that iodine is more easily liberated by oxidizing agents than either chlorine or bromine.

Iodides are found in sea water, but in much smaller quantities than bromides. Fairly large quantities of iodates, chiefly that of sodium, are found in the Chile saltpeter beds, and the greater part of the iodine of commerce is obtained from the mother liquor left in the purification of this crude sodium nitrate. The other source of iodine is from ashes of certain seaweeds gathered off the coasts of Scotland and Ireland. They were formerly the main source of iodine, and it was in their ashes that the element was discovered.

Preparation of the Element.—Iodine may be liberated from iodides by any of the oxidizing agents used for chlorine or bromine, and by some others in addition which are too feeble to serve in the other cases. A few of the equations are given below; others may be easily written by simply substituting the symbol "I" for "Cl" or "Br" in the corresponding equations for these elements:

$$4HI + O_2 = 2H_2O + 2I_2$$
$$4HI + MnO_2 = MnI_2 + I_2 + 2H_2O$$
$$2KI + MnO_2 + 3H_2SO_4 = MnSO_4 + 2KHSO_4 + I_2 + 2H_2O$$

The last reaction is very commonly used (Fig. 29).

Like bromine, iodine may be liberated by the action of chlorine strong sulfuric acid upon hydriodic acid or iodides:

$$2KI + Cl_2 = 2KCl + I_2$$
$$8HI + H_2SO_4 = 4H_2O + H_2S + 4I_2$$

Hydriodic acid is oxidized even more readily by sulfuric acid an hydrobromic is, and hence it is not possible to prepare ydriodic acid by the distillation of an odide with sulfuric acid.

Just as free chlorine will liberate free romine from hydrobromic acid or bromides, so bromine will set iodine free from the corresponding iodine compounds:

$$2KI + Br_2 = 2KBr + I_2$$

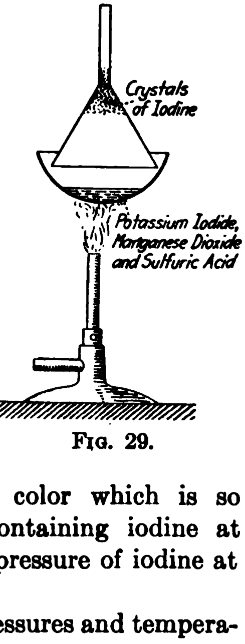


FIG. 29.

Physical Properties of Iodine.—At rdinary temperatures chlorine is gaseous, romine liquid, and iodine solid; this shows regular change in the physical state the atomic weight increases. Iodine rystallizes in large rhombic plates, having steel gray color and an almost metallic uster. It melts at 114°C., and boils at 84°C. The vapor has a beautiful violet color which is so trong that it can be seen in a bottle containing iodine at rdinary temperatures, although the vapor pressure of iodine at uch temperatures is very low.

The vapor density of iodine at ordinary pressures and temperaures below 700°C. shows a molecular weight of 254. The atomic reight of iodine is 126.92, hence the formula for iodine under hese conditions is I_2. If the temperature be raised above 700°C. he molecular weight gradually decreases until at 1,700°C. it ecomes constant again at 127 corresponding to the formula I. ise in temperature then above 700°C. has caused a reversible issociation of I_2 into I.

$$I_2 \rightleftarrows 2I$$

he color of I is different from that of I_2, and doubtless if the igh temperature did not interfere with its study I would be ound to be a strikingly different substance from I_2.

Iodine is but very slightly soluble in pure water, imparting to it a brownish color. It is much more soluble in alcohol, chloroform, and carbon disulfide than in water. The alcoholic solution is brown, while that in chloroform or carbon disulfide has the violet color of the vapor. Free iodine will dissolve in solid starch forming a solid solution having a strong blue color. This may be used as a very delicate test ther starch or iodine. In the latter case, it is carried out lows: a suspension of finely divided starch in water is prep by pouring boiling water over starch rubbed to a cream wi ittle water. Some of this is added to the solution suspect contain iodine. If the latter is free, the strong blue color o starch iodide solution at once appears. If the iodine is not t is liberated by the cautious addition of a little chlorine w

Law of Distribution.—As m oned above, iodine is much more soluble in carbon disulfide than in water. Carbon disulfide and water are not appreciably soluble in each other, and when brought together form two liquid layers, the carbon disulfide at the bottom. If now, some iodine be introduced, it will dissolve both in the water and the carbon disulfide, but to a far larger concentration in the latter. In fact, when equilibrium results it will be found that the weight of iodine per cubic centimeter in the carbon disulfide is 600 times that per cubic centimeter in the water.

This is an example of the phenomena described by the law of distribution which states that: *When two immiscible liquids are brought in contact with a third substance, soluble in each, this third substance distributes itself between the two solvents until its concentration in the one solvent bears a certain constant ratio to its concentration in the other.* In this case, the ratio of the concentration in the carbon disulfide to that in water is 600 : 1. Some substances have higher molecular weights in certain solvents than in others and this law holds only when the molecular weight of the third substance is the same in each of the solvents.

Chemical Properties of Iodine.—The chemical properties of iodine are very much like those of chlorine and bromine except that it is much less active and is not so strong an oxidizing agent. It combines directly with hydrogen and many other elements for the formation of iodides. It does not form a hydrate with water.

dine is much more soluble in solutions of iodides than in pure ater. In many ways the solution acts as though the iodine ere free, in others, it behaves as if it were in combination. his is explained by assuming the existence in the solution, of a omplex ion, I_3^- formed by the reversible reaction shown below:

$$I^- + I_2 \rightleftarrows I_3^-$$

Hydrogen Iodide.—The slight differences in the methods for the preparation of hydrogen iodide from those for hydrogen chloride nd bromide are due mainly to the fact that it is still less stable nd more easily oxidized than the latter. It may be made by he direct combination of the elements. The action is, however low, reversible, and far from complete. It is catalyzed by platinum, but this simply brings about the equilibrium quicker without changing the composition of the equilibrium mixture. At 00°C., 80 per cent. of a mixture of equal volumes of hydrogen nd iodine gases will be converted into hydrogen iodide, or 20 er cent. of pure hydrogen iodide will be decomposed; and this aseous mixture will remain unchanged in composition so long s it is kept at this temperature. If increasing pressure is put pon this system, no change will follow because as shown in the quation

$$H_2 + I_2 \rightleftarrows 2HI$$

here is no change in volume as the reaction proceeds.

As mentioned above, the preparation of hydrogen iodide by he action of sulfuric acid upon sodium iodide is excluded because of the oxidizing action of the sulfuric acid. By using hosphoric acid instead of sulfuric, hydrogen iodide may be prepared by this method.

It may be made by the action of iodine upon hydrogen compounds. An aqueous solution of hydrogen iodide may be easily btained by passing hydrogen sulfide into a suspension of iodine n water:

$$H_2S + I_2 = 2HI + S$$

The most common method for the preparation of hydrogen odide is by the interaction of iodine, phosphorus and water.

Phosphorus tri-iodide is first formed and then decomposed by water giving hydrogen iodide and phosphorous acid:

$$2P + 3I_2 = 2PI_3$$
$$PI_3 + 3H_2O = 3HI + H_3PO_3$$

This is analogous to the best method for the preparation of hydrogen bromide.

Physical Properties.—Hyd [illegible] odide as a colorless gaseous substance much heavier tha [illegible] its molecular weight is 128. It may be condensed to a [illegible] yellowish liquid, boiling at − 36°C. and freezing at − [illegible] Hydrogen iodide is very soluble in water; the soluti [illegible] rated at 0°C. contains 200 parts by weight of hydrogen [illegible] o 100 parts of water. Like hydrogen chloride and bror [illegible] forms a maximum boiling mixture with water which boils at [illegible] °C. and contains 57 per cent. hydriodic acid.

Chemical Properties.—Hydrogen iodide is the least stable of the hydro-halides and is so easily oxidized that it is an excellent reducing agent. It burns in oxygen, reacts with chlorine with a flash of light and the formation of hydrogen chloride and free iodine. The liquid is a non-conductor of electricity and is inactive chemically. But the solution in water, hydriodic acid, is an excellent conductor of electricity and is a strong acid, being as active as hydrochloric acid solution containing an equal number of gram moles per liter. When a colorless solution of hydriodic acid is exposed to the air it takes up oxygen, quickly turns brown, and finally deposits crystalline iodine. The equation is as follows:

$$4HI + O_2 = 2H_2O + 2I_2$$

It is this reaction which gives the iodine in the rare cases mentioned above in which it occurs free in nature.

Oxygen Compounds of Iodine.—The oxygen compounds of iodine are, in general, much more stable than those of bromine. They are formed in analogous ways to the corresponding compounds of chlorine. The halogen first reacts with water and a base to give an iodide and hypoiodite. The hypoiodites are even more unstable than the hypobromites, and very quickly pass over into the iodides and iodates.

It will be recalled that iodine occurs in nature largely as sodium odate in the Chile saltpeter beds.

Iodic acid may be prepared from iodates by the second general method, but is more readily obtained by the action of nitric acid upon iodine, as shown in the following equation:

$$I_2 + 10HNO_3 = 2HIO_3 + 10NO_2 + 4H_2O$$

NO_2 is called nitrogen peroxide.

Iodic acid is a stable substance which crystallizes from its very concentrated solutions in lustrous crystals which are extremely soluble in water. The solution is a strong acid. By carefully heating the crystals, they decompose into water and iodine pentoxide, I_2O_5,

$$2HIO_3 \rightleftarrows H_2O + I_2O_5$$

The action is reversible so that the pentoxide is also called iodic anhydride. Iodic acid is a fairly strong oxidizing agent and rapidly reacts with hydriodic acid to form iodine.

$$HIO_3 + 5HI = 3H_2O + 3I_2$$

Periodates and Periodic Acid.—When sodium hypochlorite in alkaline solution acts upon sodium iodate, rather difficultly soluble sodium periodate, $Na_2H_3IO_6$, separates out:

$$NaIO_3 + NaClO + NaOH + H_2O = Na_2H_3IO_6 + NaCl$$

This is the disodium salt of orthoperiodic acid, H_5IO_6, which may be easily prepared by the second general method for the preparation of acids. As will be seen, this does not correspond very closely with perchloric acid, $HClO_4$. By long and careful heating to 100°C. in a vacuum the ortho acid, H_5IO_6, loses water and passes over into the meta acid, HIO_4.

Oxides of Iodine.—Iodine forms two oxides, the tetroxide, I_2O_4, and the pentoxide, I_2O_5; the latter is iodic anhydride.

FLUORINE

The atomic weight of fluorine is 19, which is smaller than that of chlorine, and hence, logically, it should have been considered first; but, as said before, its properties are not as typical of the halogens as are those of chlorine, and consequently it was left until this point.

Occurrence.—Fluorine never occurs free in nature, in fact it is one of the most difficult of the elements to liberate. It is generally found as calcium fluoride (fluor spar), CaF_2. Two other fairly common compounds are cryolite, Na_3AlF_6, and apatite, $Ca_5(PO_4)_3F$. These are all difficultly soluble, while the most abundant of the naturally occurring compounds of the other halogens have been easily soluble.

Preparation.—As we passed from chlorine through bromine to iodine, it was noted that it became easier and easier to oxidize the compounds, and so to liberate the elements, as the atomic weight increased. This would lead us to expect that fluorine the halogen with the smallest atomic weight, would be the hardest to oxidize, and this is found to be true; in fact there is no oxidizing agent powerful enough to set the fluorine free. There remains then only one method for its preparation, electrolysi of a compound. Water must be absent because fluorine and water immediately react with the formation of hydrogen fluorid and ozone,

$$3F_2 + 3H_2O = 3H_2F_2 + O_3$$

Anhydrous liquid hydrogen fluoride is almost a non-conducto of electricity, but it dissolves potassium acid fluoride readily this salt dissociates into ions and the solution becomes a conductor. Fluorine is given off at the anode and hydrogen at th cathode. Possibly potassium is first liberated, and then react with the hydrogen fluoride,

$$H_2F_2 + 2K = H_2 + 2KF$$

The electrolysis is carried out in a copper U-tube cooled to − 2 using platinum-iridium electrodes.

Physical Properties.—Fluorine is a gas having a greenish yellow color much like that of chlorine only less intense. I liquefies at low temperatures, boils at −186° and freezes at −223 Because of the very great activity of fluorine, it is difficult t determine its density; but the molecular weight evidently is not f from 38, and since the atomic weight is 19 the formula is F_2.

Chemical Properties.—Fluorine combines with all the elemen except oxygen, nitrogen, chlorine and the members of the arg group. Hydrogen fluoride is an especially stable compound a is instantly formed when fluorine is brought in contact with hydr gen even at a temperature of −252° or with almost any hydrogen compound at ordinary temperatures. The reaction with water has been noted above. Fluorine and hydrogen chloride react for the liberation of chlorine; of course, it will react even more readily on hydrogen bromide and hydrogen iodide.

Hydrogen Fluoride.—Hydrogen fluoride containing a little water may be easily prepared by distilling a fluoride, usually that of calcium, with sulfuric acid:

$$CaF_2 + H_2SO_4 = CaSO_4 + H_2F_2$$

Here, of course, there is no difficulty caused by the oxidation of the hydrogen fluoride. But there is a complication due to the fact that hydrogen fluoride will readily attack glass, and hence the operation must be carried out in platinum or lead retorts. The anhydrous acid may be easily prepared by heating acid potassium fluoride in a platinum retort.

$$2KHF_2 \rightleftarrows 2KF + H_2F_2$$

Physical Properties.—Hydrogen fluoride is a clear colorless liquid boiling at 19°. This is exceptionally high when compared with hydrogen chloride, etc. It dissolves readily in water, and like the other hydrogen halides forms a constant boiling mixture with water. This contains 35 per cent. hydrogen fluoride and boils at 120°C. The density of hydrogen fluoride vapor, at temperatures but little above its boiling-point, shows a molecular weight of 40, corresponding to H_2F_2; at higher temperatures the density decreases, and from the boiling-point of water upward the molecular weight is 20 and the formula HF. The existence of the compound H_2F_2 is an important point of difference from the other hydrogen halides.

The formula H_2F_2 indicates a dibasic acid; that is, one a mole of which can neutralize two moles of sodium hydroxide. This is confirmed by the existence of potassium acid fluoride, KHF_2, and others of the same type. The neutral salt, K_2F_2 or KF, is also well known.

The most interesting property of hydrogen fluoride is its action on glass and other silicon compounds. When it acts on glass which contains silicates of sodium and calcium, gaseous silicon fluoride, SiF_4, and fluorides of sodium and calcium together with water are formed:

Use is made of this for etching designs on glass. The first coated with wax, the design is scratched through, an the whole exposed to the vapor or a solution of hydrogen fl Because of this action, it is of course impossible to keep fluoric acid in glass, but it may be kept in wax or gutta- bottles. The commercial acid is stored and shipped i containers.

The action of hydrofluoric acid on glass is not due to it an especially strong acid, because when we come to exam action upon metals we find that a solution containing 2 of hydrofluoric acid in 1,000 grm. of water will act muc slowly on a given piece of zinc than will a solution con 36.47 grm. of hydrochloric acid in the same amount of and yet each solution contains the same amount of hy which is capable of being replaced by a metal. The el conductivity of a normal hydrofluoric acid solution is smaller than that of normal hydrochloric acid and this in that hydrofluoric acid is much weaker than hydrochloric.

The following table gives in a condensed form a summ the more important of the properties of the halogens.

Formula of element	F_2	Cl_2	Br_2	
Atomic weight	19	35.46	79.92	12
Physical state at ordinary temperature.	gas	gaseous	liquid	
Boiling-point	−186°	−33.6°	+59°	+
Freezing-point	−223°	−102.0°	− 7.3°	+
Color	light yellowish green	yellowish green	Brown red	Gra
Oxidizing agent	strongest	very strong	strong	
Hydrogen compounds	H_2F_2-HF	HCl	HBr	
Physical state	gaseous	gaseous	gaseous	g
Boiling-point	+19°	− 83°	−68.5°	−
Freezing-point	−92.3°	−112°	−86°	−
Color	colorless	colorless	colorless	c
Solution in water	weak acid	strong acid	strong acid	str
Action toward oxidizing agents	unchanged	oxidized by strong	rather easily oxidized	ver o
Heat of formation Gaseous	161Kj.	92Kj.	35Kj.	−
Heat of formation dissolved	205Kj.	165Kj.	118Kj.	+
Heat of Neutralization NaOH	68Kj.	57Kj.	57Kj.	
Oxyacids	none	HClO $HClO_2$ $HClO_3$ $HClO_4$	HBrO .... $HBrO_3$	H .... H H

This table shows that there are regular changes in a number of the properties of these elements as the atomic weight increases. For example the boiling- and melting-points of the elements rise as the atomic weight increases. The student will gain considerable information if he follows the other properties of these elements through in the same way.

Hydrogen fluoride has an abnormally high boiling-point. In this connection, it is significant that it alone of the hydrohalides ionizes solutes and that other ionizing solvents boil higher than their inactive analogues.

Hydrolysis.—Salts of weak acids or of weak bases when in solution in water act in a very peculiar manner. Their solutions are not neutral as are those of the salts of strong acids and bases, but the salts of weak acids give alkaline, while those of weak bases give acid reacting solutions. Since the salts themselves do not contain either the hydroxyl or the hydrogen ions, which give the solutions their reactions, the question of the source of these ions is one which calls for some little explanation. Evidently they must have come from the water. But why should the hydroxyl ion appear in a solution of a salt of a weak acid, and the hydrogen ion in the salt of a weak base when neither is prominent in a solution of a salt of a strong acid and base? The theory of electrolytic dissociation furnishes a satisfactory explanation.

Pure water is a very poor conductor of electricity but it is not an absolute non-conductor. Its conductivity has been measured and indicates that water itself is dissociated to a slight extent so that 1 grm. of hydrogen and 17 grm. of hydroxyl as ion are present in eleven million liters of water. Expressing the concentration in terms of the number of gram ions per liter, the concentration of each of these substances is the same and they balance each other in their action on litmus.

Reactions between substances in the ionic condition tend to ake place in such ways that the concentrations of the ions are educed, either through the formation of substances which pass ut of solution or those which are but slightly dissociated.

When a salt of a weak acid and a strong base, say sodium hypochlorite, is dissolved in water, there are present side by side sodium, hypochlorite, hydrogen, and hydroxyl ions. Hypochlorous acid is a very weak acid, and hence, but slightly dissociated, while sodium hypochlorite is highly dissociated. There is then a chance for a decrease in the ions by the union of the hydrogen and the hypochlorite ions, and this they are assumed to do to a certain extent. The solution would then contain sodium as ion, some hypochlorite, enough hydroxyl to make up for the hypochlorite ion whic ined with hydrogen as ion, and undissociated hypochlorous . The undissociated hypochlorous acid of course does not r n litmus, while the hydroxyl ion turns litmus blue. So the so on reacts alkaline and it is evident that a salt of any other we acid should act in the same way.

When the hydrogen ion combi with the anion of the weak acid, not only is the hydroxyl left balanced in its action upon litmus, but the concentration of hydroxyl increases. This comes from more of the water's breaking up in an effort to keep up the concentration of the hydrogen. The equation for the ionization of water is

$$\begin{array}{ccccc} H_2O & \rightleftarrows & H^+ & + & OH^- \\ a & & b & & c \end{array}$$

Letting a, b and c represent the concentrations of the water, hydrogen and hydroxyl ions respectively, the Mass law equation becomes

$$\frac{bc}{a} = \text{constant}$$

Now a is constant because it stands for the concentration of a homogeneous liquid, and hence the product bc is constant and as b decreases c must increase.

Salts of weak bases and strong acids react acid because of the combination of the cation of the salt with the hydroxyl of the water with the formation of the undissociated base, thus leaving the hydrogen as ion in excess.

The phenomena which we have just been discussing are included under the name of hydrolysis. Speaking in terms of the ionic theory we may say that hydrolysis consists in the formation of an undissociated acid or base by the action of water upon a salt of a weak acid or base.

ons of salts of strong acids and bases are neutral, because nese conditions there is no tendency for either hydrogen oxyl to combine with an ion of the salt; so these salts do rolyze.

VALENCE

ormulas of some of the principal hydrogen compounds of -metallic elements are given in the following table:

HF	H_2O	H_3N	H_4C
HCl	H_2S	H_3P	H_4Si
HBr	H_2Se	......	......
HI	H_2Te	......	......

al of these compounds have not been studied as yet, but e introduced here simply to show the different types of ation. H_2S is hydrogen sulfide, H_2Se hydrogen selenide, ıydrogen telluride, H_3N or NH_3 ammonia, and H_3P ne, H_4C or CH_4 marsh gas, H_4Si silicon hydride.

this table it may be seen that these compounds fall y into four groups according to the number of atomic of hydrogen which unite with one atomic weight of the ement. *Each element is considered to have a certain com- ›ower or valence which is measured by the number of atomic of hydrogen or of an equivalent substance with which one veight of that element can unite to form a compound.* This is called the valence of the element. From the definition ıce, it follows that in the compounds given in the above luorine, chlorine, bromine, and iodine are monovalent; sulfur, selenium and tellurium divalent; nitrogen and ›rus trivalent; while carbon and silicon are tetravalent. en is our standard substance for measuring valence and is › have a valence of one or to be monovalent. Sometimes ent does not combine with hydrogen, and then of course possible to work out the valence from the hydrogen com- and in this case we must resort to some other method. these is to take a compound with some equivalent sub- *An equivalent substance is a substance one atomic weight can unite with, replace, or be replaced by, one atomic weight gen.*

An atomic weight of sodium replaces one atomic weight of hydrogen in the compound hydrogen chloride forming sodium chloride, NaCl, and is therefore monovalent; also one atomic weight of silver is replaced from silver chloride, AgCl, by one atomic weight of hydrogen, re-forming hydrogen chloride, therefore, silver is monovalent. Chlorine then in chlorides is determined to be monovalent: di [illegible] ecause it was originally combined with one atomic weigh [illegible] drogen in hydrogen chloride; indirectly because it is com [illegible] ith one atomic weight of the monovalent substances silver an [illegible] odium. Because chlorine in chlorides is monovalent, phosp [illegible] is in phosphorus trichloride, PCl_3, is trivalent, while in the p [illegible] tachloride, PCl_5, it must be pentavalent. It is not necessa [illegible] owever, that we take a compound with a substance exact [illegible] ivalent to one atomic weight of hydrogen; for once we have [illegible] ablished the valence of any given element, it may in turn be used to measure that of others. One atomic weight of oxygen is united with two atomic weights of hydrogen in the compound water, hence oxygen is divalent and is commonly used as a standard for determining valence. Take for example, phosphorous trioxide, P_4O_6; the six atomic weights of oxygen have together a valence of twelve, which is divided between the four atomic weights of phosphorus, showing that each atomic weight of the latter has a valence of three. In the pentoxide, P_2O_5, the valence of the five oxygens is ten, which is divided between the two of phosphorus; and therefore in this compound the phosphorus has a valence of five, as in the pentachloride.

The examples just given show that the valence of an element is not a fixed constant. However, the number of valences belonging to any one element is generally small. Nitrogen has an unusually large number of valences, as may be seen from the following list of its oxides, N_2O, NO, N_2O_3, NO_2, N_2O_5. In these it varies from monovalent to pentavalent. Comparatively few elements have more than two valences so that these properties are not difficult to learn, and they are of great assistance in the formulation of compounds.

Equivalent Weights.—The conception of valence enables us to get easily another useful conception, that of equivalent weight. This is the number of parts by weight of an element will combine with, replace or be replaced by 1.008 parts ight of hydrogen, or 8 parts of oxygen. Or it may be d as the atomic weight of the element divided by its e. For example, the equivalent weight of sulfur in gen sulfide is $^{32.06}/_{2}$; of nitrogen in ammonia is $^{14.01}/_{3}$; rbon in marsh gas is $^{12}/_{4}$. From the second form of the tion of equivalent weight, it is evident that an element has ny equivalent weights as it has valences.

se equivalent weights are like the atomic weights in many ts, except that they represent directly without any multiple oportions by weight in which the elements combine.

1

CHAPTER XII

S

General.—Sulfur is an elemen hich has been known since prehistoric times. It occurs fair abundantly in nature, both free and in compounds. The f ulfur is generally found in volcanic regions, but several de s of non-volcanic sulfur are known, notably those of Louis which now furnish most of the sulfur used in the United together with large quantities for export. In combinati sulfur occurs chiefly in the form of sulfates, such as gypsum, $CaSO_4 \cdot 2H_2O$, Glauber salts, $Na_2SO_4 \cdot 10H_2O$, and Epsom salts, $MgSO_4 \cdot 7H_2O$, and as sulfides, pyrite, FeS_2, zinc blende, ZnS, and galena, PbS. It is present in combination in many portions of the animal and plant organisms.

In many of its chemical properties, sulfur shows a rather close relationship to oxygen. Like oxygen it is able to assume allotropic forms, and is somewhat remarkable for the large number of such modifications which are known to exist, two and probably more crystalline modifications, two liquid, and at least two gaseous forms.

Extraction of Sulfur.—Most of the sulfur from volcanic sources comes from Sicily where it is found in large quantities mixed with limestone, gypsum, celestite and other minerals. The sulfur is extracted from the ore by heating in oven-like kilns or cells made of masonry. The greater part of the heat is furnished by burning coke which is mixed with the ore and charged into the cells. Of course, part of the sulfur burns. Economy of fuel is secured by arranging the cells in batteries of two or more and passing the gases from the one in action into a freshly charged cell in order that the waste heat from the first may warm th charge in the second. The sulfur melts and runs down to th floor of the cell from which it is drawn off and cast into conica wooden moulds forming the roll sulfur or brimstone of commerce In some more recent installations the sulfur is extracted by melt

; it out with high-pressure steam. This method is being used ;h success in some rather recently developed mines in Mexico. In Louisiana, the sulfur is obtained by drilling down about 0 ft. to the sulfur-bearing deposits and forcing down into the les water heated to a temperature of 168° which is far above e melting-point of sulfur (120°). The water must, of course, be ıder pressure of about seven atmospheres to reach this tempera-re. The sulfur melts and collects at the bottom of the hole; om there it is pumped out by compressed air. The sulfur can e obtained in this way very cheaply, and is more than 99.5 er cent. pure. A single well often yields 500 tons of sulfur per ay and the entire mine has produced 122,000 tons in two months hich is more than the world's consumption for that period. he production of sulfur in the United States in 1914 was 328,000 ng tons.

urification of Sulfur.—When it is necessary to purify roll lfur, the process of distillation is employed. The sulfur is iled in iron retorts and the vapor is condensed in large brick ambers. At first when the walls of the chamber are cool, the lfur condenses in the form of a rather fine powder, and is put the market under the name of flowers of sulfur. When the amber becomes heated from the at of condensation of the sulfur, e latter collects in the form of a quid and is drawn off into moulds before.

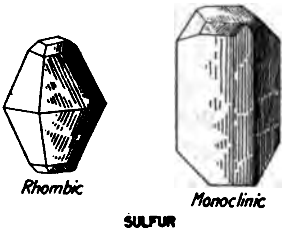


FIG. 30.

Crystalline Forms of Sulfur.—Crys-ls of rhombic (Fig. 30) or α sulfur re found in nature and may be easily epared by dissolving sulfur in car-on disulfide, in which it is readily oluble, and allowing the solution to evaporate slowly. The ulfur is deposited in octahedral-like crystals which have a ensity of 2.07, and melt to a clear yellow liquid at 113°. If he clear crystals are kept for some time at temperatures etween 100° and the melting-point they gradually become paque and brittle, and when this change is complete, will melt t 120° instead of 113°, and have a density of 1.96 instead of .07. They then have undergone a transformation into β or monoclinic sulfur (Fig. 30). This change is hastened scratching the rhombic crystals with some hard point or simply touching them with a monoclinic crystal.

Well defined crystals of monoclinic sulfur are easily obtain by melting some sulfur and allowing it to cool until a crust formed on top. A hole is then made through this, and the molten sulfur is poured out e sides and bottom of the ves will then be found covered long needle-shaped monocli crystals. When first formed crystals are amber colored, may be bent slightly without aking. If the crystals are ke at 100° or above, they retain eir properties indefinitely, if kept at ordinary temperat s for a day or so they chan color to the lemon yellow of ary sulfur, become opaque, increase in density to rt they change into α or rho bic sulfur. This transform is hastened by contact wi rhombic crystals. The external form of the crystals is th of the monoclinic, while internally they consist of an aggregati of rhombic crystals. Such crystals as these, which are internal of one form and externally of another, are called pseudomorph

Transition Point.—The facts just given indicate that the mon clinic form is stable at higher temperatures while the rhombic at lower. There must be then a temperature at which they both stable. This temperature is 96° and is called the transiti point of these modifications of sulfur. From 96° to 120° monoclinic modification is stable while the rhombic is stal below 96°.

At 96° the two modifications are in equilibrium, and hen have the same vapor pressure, solubility, etc. The monocli can exist below 96°, but in an unstable state and under these ditions it is more soluble than the rhombic and has a higher va pressure. Correspondingly, above 96° the rhombic is the stable form and has the greater solubility and vapor pressu These are simply examples of the general rule that the less sta modification has the higher solubility and vapor pressure.

Although unstable, the monoclinic sulfur can exist for a t below 96° and the rhombic above this temperature. This due to what is called suspended transformation and is m the same phenomenon as the supercooling or superheating water.

Liquid Sulfur.—Monoclinic sulfur melts at 120° to a light llow, mobile liquid, which on cooling passes back into monoinic crystals. If, however, the temperature be raised to 160° e liquid suddenly becomes dark in color and so viscous that the ssel may be inverted without the contents running out. At 0° the maximum viscosity is reached; at 260° the viscosity gins to decrease noticeably, and at 444.6°, the boiling-point of lfur, the liquid is mobile once more.

The cause of this remarkable change at 160° is the appearance a new form of liquid sulfur called μ sulfur. When the dark lored liquid is slowly cooled the reverse change takes place, and e light yellow form reappears.

Amorphous Sulfur.—By heating sulfur to temperatures near boiling-point and suddenly cooling the mass by pouring it a thin stream into water, a clear, transparent, plastic, semiid substance is obtained, which is called plastic sulfur. After few days it becomes hard and opaque and is then found to const of a mixture of rhombic crystals, soluble in carbon disulfide, d another form of sulfur which is insoluble in carbon disulfide. is not crystalline and hence is called amorphous sulfur. It is percooled sulfur, and changes slowly into the crystalline variety. he change takes years for completion at ordinary temperatures, ut is finished in an hour at 100°.

There is another amorphous modification, soluble in carbon isulfide, and also soluble in water.

Molecular Weight.—At 444.6° sulfur boils. The vapor has an range yellow color when just above its boiling-point. At 500° is a deep red and then becomes lighter until at 650° it is a light ellow. The molecular weight at temperatures near the boilingoint is 230 and gradually falls until at 1,000° it reaches 64 and mains constant at this figure as the temperature is raised. ince the atomic weight of sulfur is a trifle over 32, the molecular eight of 230 corresponds to a formula of something beveen S_7 and S_8, while that of 64 indicates a formula of S_2. he molecular weight of the element in solution as determined om the lowering of the freezing-point shows that when dislved it has the formula S_8.

Chemical Properties of Sulfur.—Most all metals when finely wdered and rubbed in a mortar with sulfur combine directly with the latter to form sulfides. At higher temperatures, combination takes place so rapidly and with the evolution o much heat that the general phenomena of combustion, the duction of light, etc., are exhibited. The element will unite with many of the non-metals; the halogens, hydro and oxygen for example.

With oxygen it forms th wo very important compou sulfur dioxide, SO_2, and sulfur ioxide, SO_3; these are the a drides of sulfurous and sulfuric acids respectively. With drogen it forms the important compound hydrogen sulfide, H

Uses of Sulfur.—Thousands f tons of sulfur are used in manufacture of sulfur dioxide which in turn is used for ma sulfuric acid, in bleaching straw, wool, feathers, etc., and germicide. Sulfur is also employed in making carbon disul gunpowder, matches, fireworks, sprays for fruit trees, vulcanized rubber.

Hydrogen Sulfide.—Hydrogen sulfide is a gaseous subst whose formula is H_2S. It occurs in nature in the gases of s volcanoes, and is found in many mineral waters, which are c monly called sulfur waters. It may be prepared by the di union of the elements by passing a stream of hydrogen through ing sulfur. The reaction is reversible and hence is not comp

Hydrogen sulfide is usually prepared by acting upon a su generally ferrous sulfide, FeS, with either dilute sulfuri hydrochloric acid. The equation is

$$FeS + 2HCl = H_2S + FeCl_2$$

The ferrous sulfide is not very soluble in water but what dissolve is largely broken up into ferrous and sulfur ions. U the addition of the acid, the sulfur ion unites with the hydr to form the very slightly dissociated compound hydrogen sul H_2S. The water soon becomes saturated with this and the substance is evolved in the gaseous state. The conditions especially favorable for reaction in this case because we ha substance formed which is both slightly dissociated, and moderately soluble. As fast as the sulfur ions present in sol are used up, more ferrous sulfide dissolves to keep up the su So the process continues until either the ferrous sulfide o acid is consumed.

Hydrogen sulfide is also formed during the decay of albuminous substances such as eggs, etc. The odor of such substances in this condition is partly due to its presence.

Physical Properties.—Hydrogen sulfide is at ordinary temperatures a colorless, gaseous substance whose molecular weight 34.09. Its critical temperature is 100°, so it can be liquefied by pressure alone at ordinary temperatures. The critical pressure is 90 atmospheres. It boils at $-61°$ and freezes at $-83°$. The liquid is chemically inactive. Hydrogen sulfide has a very disagreeable odor much like that of rotten eggs, and acts as a powerful narcotic poison when inhaled. Very dilute chlorine gas is used as an antidote.

Hydrogen sulfide is somewhat soluble in water. One volume of water dissolves 4.37 volumes at 0° and 3.23 at 15°. The solubility follows Henry's law *that the volume of a given gas dissolved by a fixed mass of a solvent is independent of the pressure, while the mass of the gas dissolved is directly proportional to the pressure.*

Chemical Properties.—Hydrogen sulfide burns in air with a pale blue flame, forming water and sulfur dioxide, SO_2,

$$2H_2S + 3O_2 = 2H_2O + 2SO_2$$

The equation shows that two volumes of H_2S require three volumes of oxygen for complete combustion. When mixed in these proportions the two gases explode violently upon the passage of an electric spark.

When the hydrogen sulfide is burned with an insufficient supply of air, water and free sulfur are the main products. This fact is taken advantage of for the recovery of sulfur from certain classes of waste products which will easily yield hydrogen sulfide.

With sulfur dioxide, hydrogen sulfide rapidly reacts, forming sulfur and water,

$$2H_2S + SO_2 = 3S + 2H_2O$$

This is probably one of the reactions which gives rise to the volcanic sulfur.

When heated to 300° it is slightly decomposed into hydrogen and sulfur, and at a white heat the decomposition is practically complete. At each temperature, there is a certain mixture of hydrogen, sulfur, and hydrogen sulfide, at which equilibrium results.

Solution in Water.—A solution of hydrogen sulfide in water acts slightly acid toward litmus, and hence is sometimes called hydrosulfuric acid. Hydrogen sulfide is a very weak acid, and is but slightly dissociated. It differs from the acids which we have discussed in detail, exc [illegible] drofluoric, in that the two atomic weights of hydrogen pe [illegible] of hydrogen sulfide are both replaceable by metals and he [illegible] e ionizable. This state of affairs is described by the term [illegible] sic, which means that one mole of the acids contains two [illegible] mic weights of replaceable hydrogen, and will react with tw [illegible] oles of a base like sodium hydroxide,

$H_2S + 2Na$ [illegible] $a_2S + 2H_2O$

Dissociation of Dibasic Acids.—Hydrogen sulfide like all other dibasic acids, shows a marked tendency to ionize in such a way that only one hydrogen per mole is split off, as shown by the following equation,

$$H_2S \rightleftarrows H^+ + HS^-$$

This ionization is especially prominent in concentrated solutions. As the solution is diluted, or still better as the concentration of the hydrogen ion is reduced by neutralization with a base, the hydrosulfide ion, HS^-, breaks up into hydrogen and sulfur as ions,

$$HS^- \rightleftarrows H^+ + S^{--}$$

As a result of this tendency of dibasic acids, it is possible to obtain two series of salts of these acids according as the one or both hydrogen ions are replaced by metals. For example, we have the compounds NaHS and Na_2S. The compound NaHS is often called sodium hydrosulfide from its resemblance to sodium hydroxide, NaOH, while Na_2S is called sodium sulfide. Several other names for the same compounds are in common use as shown by the following table:

NaHS	Na_2S
Acid sodium sulfide	Neutral sodium sulfide
Primary sodium sulfide	Secondary sodium sulfide
Mono-sodium sulfide	Di-sodium sulfide

terms acid and neutral sodium sulfide are rather deceptive, the so-called acid salt is really just about neutral in its n upon litmus, while the neutral salt is decidedly alkaline. s latter effect is due to hydrolysis which changes the neutral ide nearly completely to the acid sulfide according to the ation,

$$Na_2S + H_2O \rightleftarrows NaOH + NaHS$$

$$2Na^+ + S^{--} + H^+ + OH^- \rightleftarrows 2Na^+ + OH^- + HS^-$$

nalytical Reactions of Hydrogen Sulfide.—The sulfides of ny of the metals are very slightly soluble in water and are nsequently precipitated when hydrogen sulfide is passed into ueous solutions of their salts. For example, a solution of rcuric chloride, $HgCl_2$, gives a black precipitate of mercuric lfide, HgS, with hydrogen sulfide,

$$HgCl_2 + H_2S = HgS + 2HCl$$

$$Hg^{++} + 2Cl^- + 2H^+ + S^{--} \rightleftarrows HgS + 2H^+ + 2Cl^-$$

lts of copper, lead, bismuth, antimony, tin, and several other etals act in the same way, and their sulfides are so difficultly luble that they will be formed even in fairly acid solutions.

Other sulfides are more soluble, and require a higher concen-ation of sulfur as ion for their formation. This can be obtained taking advantage of the fact that salts of weak acids are ghly dissociated, and using instead of hydrogen sulfide, sodium ammonium sulfide. For example, ferrous sulfide is not ecipitated by hydrogen sulfide, but is by sodium sulfide,

$$Fe^{++} + 2Cl^- + 2Na^+ + S^{--} \rightleftarrows FeS + 2Na^+ + 2Cl^-$$

se is made of these properties of the sulfides to separate the etals into groups according to similarities in their behavior, d this together with the fact that many of the sulfides have stinctive colors, makes hydrogen sulfide an exceedingly im-rtant reagent.

Hydrogen Sulfide as a Reducing Agent.—An aqueous solution hydrogen sulfide when exposed to the air loses its odor and comes milky, finally depositing a white precipitate of finely divided sulfur. This is formed by the oxidation of the hydrogen sulfide by the oxygen of the air,

$$2H_2S + O_2 = 2H_2O + 2S$$

The oxygen oxidizes the hydrogen sulfide, and the latter reduces the oxygen.

When hydrogen sulfide is p[illegible] into water in which iodine is present a solution of hydrio[illegible]cid is obtained together with free sulfur,

$I_2 + H_2$ [illegible] $2HI + S$

or expressed as ions,

$I_2 + 2H^+ + S^{--}$ [illegible] $2H^+ + 2I^- + S$

In this case the action is easil[illegible]een to be between the sulf ion and the thing reduced—the iodine. Upon examination the other cases in which hydrogen sulfide acts as a reducing age it will be found that in the majority of cases the action consis in the transformation of the sulfur ion into free sulfur, but som times sulfuric acid is formed. The hydrogen has nothing to with the reducing action.

Hydrogen sulfide will reduce concentrated sulfuric acid water and sulfur dioxide, sulfur being set free,

$$H_2S + H_2SO_4 = S + 2H_2O + SO_2$$

Because of this action, concentrated sulfuric acid cannot be used to dry hydrogen sulfide.

Polysulfides.—When a solution of a soluble sulfide or acid sulfide is brought in contact with sulfur, the latter is dissolved and the solution becomes dark yellow in color. If sodium sulfide is used, compounds Na_2S_4, and Na_2S_5 may be obtained. These substances are called polysulfides. They are salts an yield ions which are Na^+ and anions which vary in compositio from S_4^{--} or HS_4^- to S_5^{--} or HS_5^-.

Sulfur Dioxide or Sulfurous Anhydride.—Sulfur dioxide, a ordinary temperatures, is a gaseous substance which is presen in the gases given off by many volcanoes. It is formed, as w have seen, by burning sulfur or hydrogen sulfide in the air. I may also be prepared by roasting metallic sulfides, pyrite, FeS for example, in the air. When these are raised to the required temperature they burn, forming sulfur dioxide, SO_2, and the oxides of the metals,

$$4FeS_2 + 11O_2 = 2Fe_2O_3 + 8SO_2$$

Many of the metals are obtained from their sulfides and such a roasting process is generally a necessary preliminary to the reduction to the metal.

Sulfur dioxide may be very conveniently prepared by the action of acids upon sulfites or acid sulfites. Under these conditions we should expect the formation of sulfurous acid, H_2SO_3, and this is doubtless formed first but breaks down into water and SO_2. The most convenient laboratory method for its preparation is based upon this, sodium acid sulfite, $NaHSO_3$, and strong sulfuric acid being used:

$$2NaHSO_3 + H_2SO_4 = Na_2SO_4 + 2SO_2 + 2H_2O$$

It is often prepared by the action of reducing agents upon concentrated sulfuric acid. The most suitable ones are perhaps metallic copper or free sulfur, the equations being:

$$2H_2SO_4 + Cu = CuSO_4 + SO_2 + 2H_2O$$

or

$$2H_2SO_4 + S = 2H_2O + 3SO_2$$

A good deal of sulfur dioxide is prepared for technical purposes by acting upon concentrated sulfuric acid with carbon,

$$2H_2SO_4 + C = 2H_2O + CO_2 + 2SO_2$$

The presence of the carbon dioxide mixed with the sulfur dioxide usually makes this method unsuitable for laboratory purposes. The greater part of the sulfur dioxide which is used in the arts is made by burning sulfur or pyrite.

Physical Properties.—Sulfur dioxide is a colorless gaseous substance with a strong odor which is familiar as the odor of burning sulfur. Its critical temperature is 156° and the critical pressure is 79 atmospheres. It may, then, be liquefied by pressure alone at ordinary temperatures. Since its boiling-point is −10°, it may be easily liquefied by a mixture of ice and salt. The liquid is as clear and colorless as water. It is a fairly good solvent and is able to ionize many salts, though to a smaller extent than water. Liquid sulfur dioxide is now an article of commerce, being sold in metal cylinders from which it may be removed as desired.

At ordinary temperatures sulfur dioxide deviates widely from the gas laws—a fact which is connected with its ease of liquefaction. It is rather soluble in [illegible]r, one volume of the latter taking up at ordinary temperature [illegible]0 volumes of sulfur dioxide and a smaller quantity at higher temperatures. At higher temperatures the solubility ap[illegible]ximately follows Henry's law. The aqueous solution smells [illegible]rongly of the dioxide which can be completely removed by [illegible]ng since it does not form either a maximum or minimum [illegible]ng mixture with water.

Chemical Properties.—Sulfur [illegible]de is stable and is decomposed only at very high temperatures. It will unite directly with chlorine for the formation of sulfuryl chloride, SO_2Cl_2, or with oxygen to form sulfur trioxide, SO_3. The solution of sulfur dioxide in water reacts acid and when neutralized with sodium hydroxide and the solution evaporated, it yields the salt, sodium sulfite, Na_2SO_3. We therefore say that the solution contains **sulfurous acid,** and ascribe to this the formula H_2SO_3. A pure acid of this composition cannot be prepared since it breaks down into water and sulfur dioxide as the solution is concentrated. Because of the formation of sulfurous acid, sulfur dioxide is often called sulfurous anhydride.

Like hydrogen sulfide, sulfurous acid is a dibasic acid and yields acid and normal salts. It is a stronger acid than hydrogen sulfide, and the normal salts are not so highly hydrolyzed as the normal sulfides. The hydrolysis, however, is marked.

Reducing Action.—Sulfurous acid and the sulfites are strong reducing agents, passing into sulfuric acid or sulfates. As an example, we may take the reaction of sulfurous acid upon chlorine and water,

$$H_2SO_3 + Cl_2 + H_2O = H_2SO_4 + 2HCl$$

Here the oxygen necessary for the formation of sulfuric acid comes from the water. The sulfurous acid may be replaced by sulfites.

Because of this reaction between chlorine and sulfurous acid, sulfurous acid and sulfites are used as "antichlors" in the bleaching industries to remove the last of the chlorine.

Sulfites are spontaneously oxidized by the oxygen of the air, an action which may be greatly slowed down by the addition of small quantities of sugar, alcohol, or glycerine, which act as negative catalyzers.

Bleaching Action.—Sulfurous acid and its salts are rather powerful bleaching agents and are extensively used for bleaching silk, wool, feathers, straw, etc., which would be destroyed by chlorine or hypochlorous acid. The sulfurous acid acts very differently from the chlorine in that it reduces the coloring matter instead of oxidizing it. The coloring matters are not destroyed in this case and after the process is finished the goods must be carefully washed to remove the altered coloring matter, as otherwise the oxygen of the air would soon restore the color. If sulfur dioxide is used, the goods are first moistened so that sulfurous acid may be formed.

Action on Organisms.—Sulfur dioxide, sulfurous acid and sulfites are powerful poisons toward vegetable organisms of all kinds. Because of this property, sulfur dioxide is used as a germicide and fungicide. Sulfurous acid and sulfites have been much used as preservatives in food products, but are now generally forbidden.

Sulfur Trioxide or Sulfuric Anhydride.—Sulfur trioxide is formed by the direct union of sulfur dioxide and oxygen,

$$2SO_2 + O_2 \rightleftarrows 2SO_3$$

The action, however, takes place very slowly even at somewhat elevated temperatures. In this case, one cannot resort to raising the temperature to a very high point in order to increase the rate of combination, because of the fact that at a high temperature the action is reversed. However, there are several substances, notably finely divided platinum and ferric oxide, Fe_2O_3, which will actively catalyze the union of the gases. In the case of the finely divided platinum, the process takes place to the best advantage when the temperature is about 400°. The sulfur trioxide so formed may be condensed to a colorless mobile liquid which boils at 46°. When cooled, it forms a transparent glassy solid which *melts* at 15°. After standing for some time, it passes over into a more stable form which appears as a white, opaque, glistening mass of needle-shaped crystals. This opaque form does not melt, but at 50° passes directly into the vapor which upon being cooled condenses to the liquid, from which the ice-like solid may first be obtained and then finally the opaque form. The white, crystalline solid has the formula S_2O_6, while that of the other m[illegible]fication is SO_3. The S_2O_6 is called a polymer of the SO_3. [illegible] formation of the liquid and glassy solid before the appearance of the stable opaque form is another instance of the phenom[illegible] described by the law of successive reactions.

Action on Water.—When sul[illegible] trioxide comes in contact with moist air, it forms dense [illegible]e fumes, consisting of sulfuric acid formed by the union [illegible]e sulfur trioxide with water vapor. When the trioxide is brought in contact with water, combination takes place with the production of so much heat that it hisses as though a red hot body were plunged into the water. The result of this action is sulfuric acid, so sulfur trioxide is often called sulfuric anhydride.

Sulfuric acid is an exceedingly important chemical as may be seen from its yearly production which amounts to over 2,000,000 tons in this country alone. It is made by two processes. The first, called the contact process, is very simple in theory, but has certain practical difficulties, and is best adapted to the production of very concentrated acid.

The second is the lead chamber process, the chemistry of which is more complex but whose operation is sure and simple. This turns out immense quantities at a low cost of a somewhat dilute acid suitable for many purposes, the bulk of it being used for preparing phosphate fertilizer.

The starting-point in each process is the preparation of sulfur dioxide either by burning sulfur in the air or more commonly by roasting a sulfide such as pyrite, FeS_2; in the latter case the reaction is,

$$4FeS_2 + 11O_2 = 2Fe_2O_3 + 8SO_2 \qquad (1)$$

In each process with the aid of catalyzers this sulfur dioxide, oxygen of the air and water are then caused to react for the formation of sulfuric acid. The chemistry of the contact process ry simple. Three reactions in addition to that in equation re involved: First the formation of sulfur trioxide,

$$2SO_2 + O_2 \rightleftarrows 2SO_3 \qquad (2)$$

nd, the union of the sulfur trioxide with sulfuric acid to fuming or pyrosulfuric acid, $H_2S_2O_7$

$$SO_3 + H_2SO_4 \rightleftarrows H_2S_2O_7 \qquad (3)$$

rd, the dilution of this fuming acid with just enough water nake the product 100 per cent. sulfuric acid

$$H_2O + H_2S_2O_7 = 2H_2SO_4 \qquad (4)$$

The reaction between sulfur dioxide and oxygen (2) is the ublesome one. It is slow, reversible, and far from complete temperatures above 400°. Because of its slowness a positive talyzer, either platinum or ferric oxide, must be used. Platim works rapidly at 400°, and at this temperature 98–99 per nt. of the SO_2 may be oxidized to trioxide.

But the platinum is quickly "poisoned" by the small quantities arsenic compounds present in the dust from the sulfur or

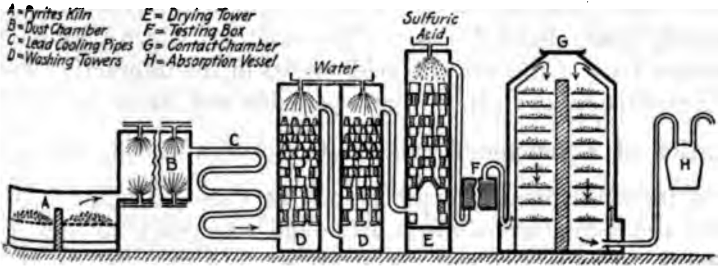


FIG. 31.

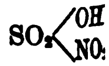
rite burners, and soon loses its activity as a catalyzer unless e sulfur dioxide is purified with painful care by first allowing e dust to settle (Fig. 31), then cooling the gas, washing it with pray of water and drying with sulfuric acid before it goes to catalyzer in the contact chamber. Ferric oxide is not isoned by arsenic but works rapidly enough only at temratures of 625° or higher, and at 625° not more than 70 per t. of the dioxide can be converted into trioxide. Hence ric oxide is much less efficient than the more expensive and troublesome platinum, so platinum is the catalyzer most commonly used. The plant is shown diagrammatically in Fig. 31. The reaction represented by equation (1) takes place in A; by equation (2), in G; and (3), in H; where the sulfur trioxide, removed from the nitrogen and oxygen left from the air by absorption in concentrated sulfuric acid, forms fuming sulfuric acid, which upon (lfuric acid as shown in (4).

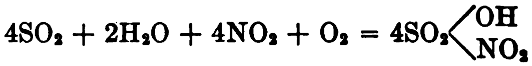
Lead Chamber this very important process, nitrogen peroxide the formation of sulfuric acid from the sulfur d ld water.

The sulfur dioxid before, see equation (1). Th oxygen comes from nitrogen peroxide, NO₂, com from the action of nd water upon nitric acid, gi ing sulfuric acid ar NO; the latter then reacts wi the oxygen of the air ygen peroxide. The equatic are as follows:

$$3SO_2 + 2HNO_3 + 2H_2O = 3H_2SO_4 + 2NO$$

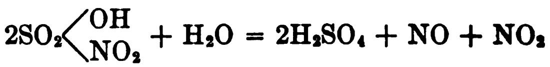
$$2NO + O_2 \rightleftarrows 2NO_2$$

The water is introduced either in the form of steam or as a spr of very finely divided water. The reactions which produce t greater part of the sulfuric acid consist in the interaction of th sulfur dioxide, oxygen, nitrogen peroxide and water for the for mation of a compound called nitrosylsulfuric acid,  $SO_2\langle{}^{OH}_{NO_2}$ and its subsequent decomposition by water, forming sulfuric acid and a mixture of nitric oxide and nitrogen peroxide. The equations are



$$4SO_2 + 2H_2O + 4NO_2 + O_2 = 4SO_2\langle{}^{OH}_{NO_2} \qquad (7$$

and



$$2SO_2\langle{}^{OH}_{NO_2} + H_2O = 2H_2SO_4 + NO + NO_2 \qquad (8$$

The nitric oxide then reacts with some more oxygen as show in equation (6) to reform the peroxide which will at once rea with more of the sulfur dioxide, oxygen, and water to form mo nitrosylsulfuric acid, which is decomposed by water, formin another lot of sulfuric acid and reproducing the oxides of nitroge cycle of changes goes on until all but one-half a per cent. of ulfur dioxide is used up. So a very small quantity of the s of nitrogen will transform a large amount of sulfur dioxide. e reactions take place in very large lead lined rooms or ıbers (Fig. 32), of which there are three or more in each :. These chambers are often 100 ft. or more in length hold from 150,000 to 200,000 cu. ft. Lead is used in their truction because it is but little attacked by dilute sulfuric The sulfuric acid formed collects on the bottom of the

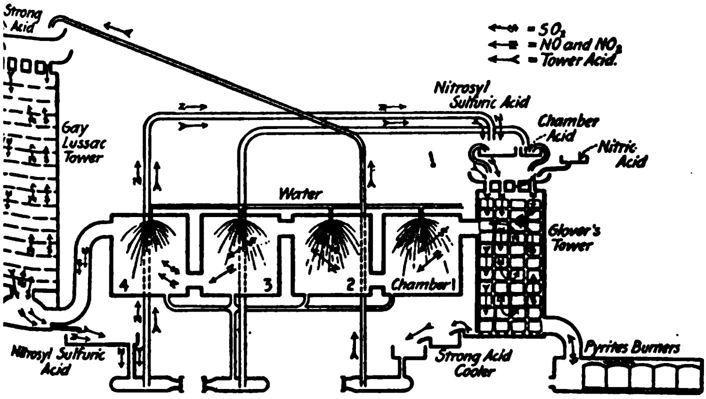
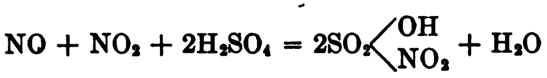


FIG. 32.

ıbers, while a mixture of the oxides of nitrogen and the gen from the air which furnished the oxygen issues from ast chamber. The oxides of nitrogen are too valuable to st so advantage is taken of the fact that they may be ab-d in concentrated sulfuric acid forming nitrosylsulfuric acid,



$$NO + NO_2 + 2H_2SO_4 = 2SO_2\begin{matrix}\diagup OH\\ \diagdown NO_2\end{matrix} + H_2O \qquad (9)$$

it will be noticed, is equation (8) written reversed. The ption takes place in what is called the Gay Lussac tower. is about 50 ft. high and is filled with tiles over which con-ated sulfuric acid runs in a thin stream, while the gases the last lead chamber enter at the bottom and leave near op. The acid, which collects at the bottom of the tower, ins the nitrosylsulfuric acid in solution. This may be easily decomposed by water, regenerating the oxides of nitrogen necessary for catalyzing the formation of the sulfuric acid. But to be of service, these oxides of nitrogen must be reintroduced into the first lead chamber. This is done by elevating the acid drawn off from the bottom of the Gay Lussac tower, with compressed air to the top of a similar structure called the Glover's tower which just precedes the first lead chamber. Here the concentrated sulfuric acid is mixed with dilute acid from the chambers. This partly decomposes the nitrosylsulfuric acid. (See equation 8). The mixture is then allowed to flow slowly down through the tower over the acid-resisting stones or tiles. On its way down it meets the hot sulfur dioxide and air from the burners. These gases enter at the bottom of the tower, pass up through and out near [illegible]op, going from there into the first lead chamber. The hot gases while flowing through the tower remove the oxides of nitrogen from the diluted sulfuric acid and evaporate a large part of the water. This returns the oxides of nitrogen to the point where they are needed, concentrates the sulfuric acid, and at the same time cools the gases to the temperature favorable for the reactions.

Other reactions than the ones given above take place during the process, whereby a part of the nitrogen compounds are reduced to nitrous oxide, N_2O, and, as this takes no further part in the reaction, it constitutes a loss of active nitrogen to the system. To make up for this and for mechanical losses, it is necessary to use about 4 parts of sodium nitrate for every 100 parts of sulfur burned, to make nitric acid enough to replace the oxides of nitrogen lost. The nitric acid is usually added at the top of the Glover's tower and here reacts with the sulfur dioxide as shown in equation (5).

The whole process may be briefly summed up as follows: Sulfur dioxide is formed in the pyrite burner, equation (1). The hot gas passes either directly to the Glover's tower or sometimes first through a dust-settling chamber. In the Glover's tower the oxides of nitrogen are removed from the nitros[illegible] sulfuric acid, equation (8), losses replaced by the additi[illegible] of nitric acid, equation (5), and part of the chamber acid concentrated. In addition, reactions represented by equations (6), (7), and (8) take place to a certain extent in the tower. From over's tower, the gases pass on through the lead chambers in the principal reactions are represented by equations (6), (7), 3). From the last chamber, the residual gases pass through ay Lussac tower where the oxides of nitrogen dissolve in oncentrated sulfuric acid, forming nitrosylsulfuric acid own in equation (9). The nitrosylsulfuric acid then goes to the Glover's tower and the oxides of nitrogen begin ourney once more.

ncentration of the Acid.—The chamber acid from the uric acid plant runs about 65 per cent. acid and 35 per cent. r. Enormous quantities of it are used at this strength, for nple, in making fertilizer, but for many purposes the greater of the water must be removed. This is very commonly done unning the chamber acid together with that from the Gay sac tower through the Glover towers until the acid has reached ncentration of 78 per cent. or higher. It may then be concentrated still further by heating in cast-iron retorts, because uric acid of this strength or stronger does not attack iron, le the weaker acid does. An entirely adequate explanation his behavior is lacking.

tills of glass or of platinum lined with gold are sometimes d instead of the cast-iron ones.

nother method of concentration which is sometimes used o evaporate the chamber acid in lead pans heated from ve until the acid has a density of 1.71 corresponding to per cent. acid, when it becomes a strong enough oxidizing nt to attack the lead rapidly. Further concentration st then be done in cast-iron, glass, or platinum.

hysical Properties.—Commercial sulfuric acid or oil of vitriol a density of 1.83–1.84 and contains 94 per cent. of the acid. e strongest sulfuric acid which can be secured by evaporation a density of 1.841 and contains 98.2 per cent. of the acid. is is the composition of the maximum boiling mixture. It s at 330° C. The vapor consists largely of a mixture of sulfur xide and water as may be demonstrated by the fact that sk filled with sulfuric acid vapor will lose water more rapidly diffusion than it does the more dense sulfur trioxide. When centrated sulfuric acid is cooled to a low temperature, crystals he pure acid, H_2SO_4, separate. These melt at 10.5°.

Aqueous Sulfuric Acid.—The heat of solution of one mole of sulfuric acid in a great deal of water is 75 Kj. So when sulfuric acid is mixed with water a great amount of heat is evolved. The acid should always be poured into the water, as otherwise so much heat is likely to be developed at one point that some of the water will be suddenly converted into steam, causing the sulfuric acid to spatter.

When concentrated sulfuric a l is mixed with water considerable contraction occurs so the total volume is less than the sum of the volumes of th er and the acid. The greatest contraction takes place whe diluted acid has a composition of 70 per cent. A total volu of 100 c.c. before the mixing becomes about 97 after the s n of the acid and cooling.

The vapor pressure of w rom aqueous solutions of the acid varies continuously with composition, and is very small indeed at ordinary temperatures from the more concentrated acid. Upon this fact depends the usefulness of concentrated sulfuric acid for drying gases.

Dissociation of Sulfuric Acid.—Pure concentrated sulfuric acid is not a good conductor of electricity, but when the acid is dissolved in water it becomes a very good conductor indeed. It is a dibasic acid, and like all others of its class, dissociates in two ways. In the more concentrated acid, the principal anion is HSO_4^-, but as the acid is diluted this breaks down to give H^+ and SO_4^{--}. As has been pointed out, it is a strong acid, but not so strong as hydrochloric.

Applications of Sulfuric Acid.—Enormous quantities of sulfuric acid are used in the arts. The largest single use is in the manufacture of fertilizers. A great deal is used in making sodium carbonate. In fact, there is scarcely a manufacturing industry of any importance which does not directly or indirectly make use of sulfuric acid.

Its many applications depend mainly upon the following facts. It is cheap, a fairly strong acid, a moderately strong oxidizing agent, not very volatile and forms slightly soluble salts with several cations. As an acid it is much used, for example, in the preparation of hydrogen, to dissolve the "scale" or coating of oxide from metal plates before further treatment in various manu processes and in the preparation of other acids from s.

age is taken of its oxidizing power in the separation of m gold in the process of refining of these metals. The xidized to silver as ion, which then forms silver sulfate, sulfuric acid is reduced to water and sulfur dioxide. is not attacked.

$$2Ag + 2H_2SO_4 = Ag_2SO_4 + SO_2 + 2H_2O$$

tensive use in the manufacture of hydrochloric and ds by the first general method depends upon its slight , which more than makes up for the fact that sulfuric aker than many of the acids which it is used to prepare. t solubility of the sulfates of barium, lead, and calcium very useful in the preparation of acids by the second ethod. In fact, its use in preparing fertilizers depends fact that it can convert calcium phosphate into easily hosphoric acid or else calcium acid phosphate and soluble calcium sulfate.

s.—Since sulfuric acid is a dibasic acid, it forms two salts, acid and neutral sulfates; for example, sodium ate $NaHSO_4$ and sodium neutral sulfate Na_2SO_4. Sul- l is a strong enough acid to make the names appropriate he acid salt actually is acid and the neutral salt, neutral. ous sulfates will be discussed in some detail under the metals.

ication.—Barium sulfate is exceedingly slightly soluble , since it requires more than 300,000 times its weight for solution. It is promptly formed whenever a solution um salt, barium chloride, $BaCl_2$, for example, is added tion of a sulfate or of sulfuric acid. This then is a of the sulfate ion. The barium sulfate is white, and ssolved in dilute hydrochloric acid, and by this is dis- d from all other barium salts, except barium selenate.

OTHER OXYGEN ACIDS OF SULFUR

furic Acid.—It will be recalled that when dilute sulfuric lectrolyzed, hydrogen and oxygen are given off in the n for the formation of water.

When 50 per cent. sulfuric acid is electrolyzed, using a ve small anode and keeping the solution cold, but little oxyg appears at the anode. At the same time a new substan persulfuric acid, $H_2S_2O_8$, is formed in the solution. The form tion of this acid is easily understood. Sulfuric acid as concen trated as 50 per cent. or more contains principally the ions H and HSO_4^-. Two ionic weight [illegible]f HSO_4^- give up their charg to the anode and at once un[illegible] form $H_2S_2O_8$. If potassium o ammonium acid sulfate, K[illegible]r NH_4HSO_4, is used instead o the sulfuric acid, the rather [illegible]ultly soluble potassium or am monium persulfate soon sepa[illegible] around the anode. These salt are now common commercial [illegible]icles, and find fairly extensiv use because they are good ox[illegible]ng agents.

Hyposulfurous Acid.—The [illegible] of this acid $H_2S_2O_4$ are forme by the action of zinc upon solutions of acid sulfites containi an excess of sulfur dioxide, or upon sulfur dioxide in soluti in absolute alcohol. Sodium hyposulfite, $Na_2S_2O_4$, is a comme cial article which is extensively used in dyeing.

The hyposulfites are less powerful reducing agents than zi but being soluble are much more rapid in their action.

Thiosulfuric Acid.—It will be recalled that a sulfite in soluti will slowly take up oxygen from the air, passing into a sulfat In much the same way, but more rapidly, a sulfite, say sodiu sulfite, will take up sulfur forming a thiosulfate, or a sulfate which one atomic weight of sulfur takes the place of an atom weight of oxygen. This is one of the ways in which sulfur sho its analogy to oxygen,

$$Na_2SO_3 + S = Na_2S_2O_3$$

The salt $Na_2S_2O_3{\cdot}5H_2O$ is known as sodium thiosulfate or inc rectly as sodium hyposulfite or "hypo." It is the most importa of the thiosulfates and is much used in photography. It i good reducing agent and is often used as such in place of sulfi For example, it may be used as an antichlor for the remova chlorine from bleached goods,

$$H_2O + Na_2S_2O_3 + Cl_2 = Na_2SO_4 + 2HCl + S$$

The protective masks worn by the soldiers in the Europ war to minimize the effect of the "asphyxiating gas," chlor wet with a solution of sodium thiosulfate and carbonate, quation given above represents the main reaction.

iosulfuric acid is so unstable that it decomposes almost as as it is liberated, into sulfur and sulfurous acid. So that olution of thiosulfate is acidulated it will become milky t at once. This decomposition is largely prevented by ddition of sulfites.

logen Compounds of Sulfur.—When dry chlorine gas is d over heated sulfur, the twoel ements combine with the tion of sulfur monochloride S_2Cl_2, which is a reddish-yellow l boiling at 138°. It is a very good solvent for sulfur and is reason has been used in vulcanizing rubber. With water, cts for the formation of sulfur, hydrochloric acid, sulfurous and thiosulfurous acid.

th bromine and iodine, sulfur forms compounds correspond- the monochloride. They are the monobromide, S_2Br_2, and oniodide, S_2I_2. Fluorine and sulfur combine so vigorously they catch fire at ordinary temperatures forming sulfur luoride, SF_6.

furyl Chloride.—Sulfur dioxide and chlorine combine ly to form sulfuryl chloride, SO_2Cl_2. The combination place much more rapidly in the sunlight than in diffused ght and is catalyzed by camphor. It is a colorless mobile l, boiling at 69°, and having a density of 1.67. With water cts to give sulfuric and hydrochloric acids,

$$SO_2Cl_2 + 2H_2O = H_2SO_4 + 2HCl$$

sitive and Negative Valence.—Hydrogen and chlorine in ogen chloride as we have learned are both monovalent. n the compound is dissolved in water it dissociates into nonovalent hydrogen ion carrying one positive charge, and nonovalent chlorine ion carrying a negative charge. This at gives the conception of positive and negative valence, and xplanation of the valence of an ion, which then becomes ical with the number of positive or negative charges which on carries. Thus the sulfur ion, S^{--}, is negative and is ent, as is also the sulfate ion, SO_4^{--}. We may, then, say the sulfate ion unites with two atomic weights of hydro- r sodium as ion; because each of these carries one positive charge or is monovalent, and two are required to neutralize the charge upon the sulfate ion and to form sulfuric acid or sodium sulfate, both of which are electrically neutral. The subject of the valence of ions is simple, and this has led to attempts to ascribe the phenomena connected with valence in general to an electrical origin. In accordance with this view, the elements, even in compounds, which are [illegible]t salts, are supposed to be charged, some positively and [illegible] negatively and the valence of each element is supposed to [illegible] determined by the number of + or – charges which it c[illegible] per atomic weight. This view seems to be not entirely [illegible]om contradictions and may be incorrect, but it is in agreem[illegible] with the facts in the great majority of cases and is a very [illegible]ful conception. According to this hypothesis, the oxygen in w[illegible]r and most other compounds carries two, the nitrogen in amm[illegible]ia three, and the carbon in methane, CH_4, four negative charges.

While it is very easy to decide that the valence of the sulfate ion is two, it is not so easy to answer the question "What is the valence of the sulfur in this ion?" If we assume that oxygen in compounds always has the valence that it has in water, viz., two negative, we may reach a reasonable conclusion in this and similar cases. Since the sulfate ion as a whole carries two negative charges, it follows that the algebraical sum of the positive and negative charges upon the sulfur and the oxygen must be -2 or $x + a = -2$, where "x" represents the charges upon the sulfur, and "a" those upon the oxygen. Now from the assumption which we have made about the valence of oxygen, each atomic weight of this element carries two negative charges, and the four would then total eight negative charges, and in the equation given above, "a" would have the value -8

$$x - 8 = -2$$

or

$$x = +6$$

From this it follows that the valence of the sulfur in the sulfate ion or in sulfuric acid for that matter, is +6. This is confirmed by the fact that sulfuric acid is so simply formed from water and sulfur trioxide SO_3, in which the sulfur evidently has a valence of +6. Working in this same way, it is easy to show that lorine in chloric acid, $HClO_3$, has a valence of +5, in chlorite, $NaClO_2$, of +3, and that the phosphorus sphoric acid, H_3PO_4, has a valence of +5. Nitrogen in nia NH_3, and in the ammonium ion NH_4^+, seems to have a e of −3; while in nitric acid HNO_3, it is +5, so it would that the valence of an element can not only change in but even in sign.

valence of a free element is considered to be zero.

lation and Reduction.—Oxidation and reduction processes een frequently mentioned in what has gone before, but ot been discussed in detail. While oxygen is the typical ng agent, attention has been called a number of times to t that we have well marked cases of oxidation into which does not enter in any way. Similarly hydrogen is the l reducing agent, but a great many reduction processes own which do not involve this element.

udy of these processes soon shows that they always produce s in the valence of the elements oxidized or reduced. his is so may be easily seen from the table given below. inspection of the last three columns in the first table will hat oxidation is always accompanied by an increase in the r of positive charges upon the element oxidized, a decrease ative being of course equivalent to an increase in the e charges. The corresponding columns of the second table te that reduction involves a decrease in the number of

TYPES OF CHANGES WHICH ARE CONSIDERED OXIDATION

tance ised	Oxidising agent	Substance formed	Valence of the oxidised substances		Change in valence
			Before	After	
	O_2	MgO	0	+2	+2
	H^+	Zn^{++}	0	+2	+2
	$KClO_3$	IO_3^-	0	+5	+5
+	Cl_2	Fe^{+++}	+2	+3	+1
	MnO_2	Cl_2	−1	0	+1
	I_2	S	−2	0	+2
	$Br_2(H_2O)$	SO_4^{--}	−2	+6	+8
--	O_2	SO_4^{--}	+4 (of S)	+6 (of S)	+2

TYPES OF CHANGES WHICH ARE CONSIDERED REDUCTION

Substance reduced	Reducing agent	Substance formed	Valence of the reduced substance		Chang in valenc
			Before	After	
Cu^{++}	Zn	Cu (metal)	+2	0	−2
Ag^+	H_2	[illegible]al)	+1	0	−1
I_2	S^{--}	[illegible]	0	−1	−1
NO_3^-	Cu	NO	+5 (N)	+2 (N)	−3
NO_3^-	Al (in KOH)	NH_3	+5	−3	−8
ClO_3^-	SO_3^{--}	Cl^-	+5	−1	−6
O_2	Mg	O^{--}	0	−2	−2

positive or an increase in the [illegible]ber of negative charges upo the element reduced. The m[illegible]eneral conception of oxidatio and reduction then is that *oxidation consists in an increase in th number of positive charges upon the element oxidized or wha amounts to the same thing, a decrease in the number of negati charges. Reduction consists in a decrease in the number of positi charges upon the element reduced, or what amounts to the sam thing, an increase in the number of negative charges.* Oxidatio and reduction are opposed processes, and one of them canno take place without the other occurring simultaneously an to the same extent. This will be seen by examining the abov table more closely. In each of these reactions, there is a oxidizing agent and a reducing agent, and in every case the on loses exactly as many charges as the other gains.

CHAPTER XIII

SELENIUM AND TELLURIUM

Selenium and tellurium are two elements which bear about the same relation to sulfur that bromine and iodine do to chlorine. The resemblance of tellurium to sulphur is perhaps less marked than that of iodine to chlorine, but selenium furnished fully as close a match for sulfur as bromine does for chlorine. A comparison of the atomic weights of the members of these two groups of elements is of some interest.

Chlorine	35.46	Bromine	79.92	Iodine	126.92
Sulfur	32.06	Selenium	79.20	Tellurium	127.50

From this it is seen that the atomic weights of sulfur, selenium, and tellurium correspond closely to those of chlorine, bromine, and iodine respectively. In each group of these elements it becomes easier to liberate an element from its hydrogen compound, the greater the atomic weight of the element is. Selenium and tellurium correspond to bromine and iodine in that they do not occur abundantly in nature although they are rather widely distributed.

SELENIUM

Selenium occurs in nature both free and combined. In the free state it is found as an impurity in crystals of native sulfur, while the compounds are usually associated with the corresponding sulfur compounds. The element was discovered in the flue dust of a sulfuric acid factory, and this together with the anode mud of electrolytic lead and copper refineries is still the chief source of the element.

Properties.—Like sulfur, selenium takes on a number of forms; amorphous, crystalline and metallic. Amorphous selenium is black and glassy unless finely powdered when it is red. There are two kinds of red crystalline selenium; they melt at

170°–180° and are soluble in carbon disulfide. If kept at 150° for some time, they change into a gray crystalline modification melting at 217° and boiling at 690°. This gray form has some metallic properties and is a poor conductor of electricity in the dark, but much better in the light. This is the basis of the selenium cells which find practical application in automatically turning on signal lights at the [illegible] of darkness. Above 1,400° the molecular weight corresp[illegible] the formula Se_2; at lower temperature the molecule is more complex.

Chemical Properties.—Selenium combines directly with iron and many other metals, and also with hydrogen, oxygen and the halogens. As a rule these compounds are formed less readily than the corresponding [illegible]fur compounds, and from them the element is more easily [illegible]erated than is sulfur from its compounds. These relations are about the same as those between bromine and chlorine.

Hydrogen Selenide.—The methods for the preparation of hydrogen selenide, H_2Se, are very similar to those for hydrogen sulfide. It may be formed by the direct union of the elements or by acting upon ferrous selenide, FeSe, with hydrochloric acid.

$$FeSe + 2HCl = H_2Se + FeCl_2$$

Hydrogen selenide resembles hydrogen sulfide in that it is a colorless poisonous gaseous substance soluble in water, giving an acid solution from which the element is deposited upon exposure to the air and further that it precipitates difficultly soluble selenides from solutions of salts of the heavy metals.

It is more easily liquefied (boiling-point −41°) than hydrogen sulfide and has a much worse odor resembling decayed horseradish.

Selenium Dioxide and Selenious Acid.—Selenium burns in air forming solid selenium dioxide, SeO_2, which will dissolve in water forming easily soluble crystalline selenious acid.

It is a weak dibasic acid resembling sulfurous acid. Like the latter it acts both as a reducing and an oxidizing agent, but differs in that its oxidizing power is much stronger than its reducing. It oxidizes sulfurous acid to sulfuric,

$$H_2SeO_3 + 2H_2SO_3 = 2H_2SO_4 + Se + H_2O$$

but reduces permanganate, being oxidized to selenic acid, H_2SeO_4,

$$4H_2SeO_3 + 2KMnO_4 = 3H_2SeO_4 + K_2SeO_4 + Mn_2O_3 + H_2O$$

Selenic Acid.—There is no selenium compound corresponding to sulfur trioxide, but selenic acid is strictly analogous to sulfuric acid.

It is in general a more powerful oxidizing agent than sulfuric acid since it liberates chlorine from hydrochloric acid and dissolves gold, but curiously enough, it is without action upon either hydrogen sulfide or sulfur dioxide.

TELLURIUM

Tellurium is decidedly rare. It occurs free but mostly as tellurides of gold, silver, lead and bismuth. Tellurium is more metallic in its characteristics than the other members of the sulfur family. It forms both amorphous and crystalline modifications; the latter has a silvery white metallic luster, a density of 6.3, melts at 450°, and boils at 1,390°. At 1,750° the molecular weight shows that the formula is Te_2. The crystalline modification is a slight conductor of electricity. The element combines directly with oxygen, the halogens and many of the metals.

Hydrogen Telluride.—Tellurium compounds are in general similar to those of sulfur and selenium, but differ in some important points.

Hydrogen telluride is prepared much as hydrogen sulfide and selenide are. It is colorless, gaseous, has a bad odor, boils higher (0°) than they, and is much less stable. Its solution in water is very feebly acid.

Tellurium Dioxide.—Tellurium burns in oxygen forming the dioxide which is a white, crystalline substance, slightly soluble in water. The solution does not redden litmus.

Tellurous Acid.—Tellurous acid, H_2TeO_3, is a white powder, slightly soluble in water but dissolved by either potassium hydroxide or strong acids. It then acts both as a base and as an acid, but is neither strongly acid nor basic; nothing which acts in both these ways is ever strong in either.

Tellurium trioxide, (TeO_3) is known, but unlike sulfur trioxide it is totally indifferent toward water. Telluric acid (H_6TeO_6 or $H_2TeO_4{\cdot}2H_2O$), is a very weak acid with some basic properties.

It is a powerful oxidizing agent and, unlike selenic acid, attacks hydrogen sulfide or selenide.

THE SULFUR FAMILY

	Sulfur	Selenium	Tellurium
Formula	[illegible]	Se_8–Se_2	Te_2
Melting-point	[illegible]	217°	450°
Boiling-point	[illegible]	690°	1,390°
Hydrogen compounds	[illegible]	H_2Se	H_2Te
Melting-point	[illegible]	−68°	−48°
Boiling-point	[illegible]	−41°	0°
Oxidized	[illegible]	Very easily	Most easily
Dioxide	[illegible]	SeO_2	TeO_2
State	[illegible]	Solid	Solid
Acid	[illegible]	H_2SeO_3	H_2TeO_3
State	[illegible]	Solid	Solid
Reducing agent	Good	Weak	Weak
Oxidizing agent	Weak	Strong	Strong
Trioxide	SO_3	....	TeO_3
Acid	H_2SO_4	H_2SeO_4	H_6TeO_6
Oxidizing agent	Fair	Strong	Strong

CHAPTER XIV

NITROGEN

eneral.—The element nitrogen occurs in nature both free l in combination. The free element is found in the air of ich it constitutes approximately four-fifths by volume. The ater part of the remainder is oxygen. The element is de- dly inactive, but its compounds are among the most reactive hemical substances. This will be seen at once when it is tioned that they include gun cotton, nitroglycerine, and ost all of our modern high explosives. The inorganic com- nds of nitrogen which occur in nature are principally am- ia, ammonia compounds, and salts of nitric acid. Large ntities of very complex carbon compounds of nitrogen are sent in coal. Nitrogen compounds are of great importance us, since it is with them that the vital phenomena seem to directly connected. The albuminoids constitute an impor- t class of such compounds, and contain almost 15 per cent. itrogen.

reparation of the Element.—Impure nitrogen containing the nbers of the argon group can be obtained from air by burning sphorus in the latter; or a product answering for many com- cial purposes may be secured by the fractional distillation of id air; but the pure element can be obtained only by decom- ing some nitrogen compound.

mmonium nitrite, NH_4NO_2, when gently heated decomposes water and nitrogen.

$$NH_4NO_2 = N_2 + 2H_2O$$

monia and copper oxide, or nitric oxide, NO, and copper t at higher temperatures and yield pure nitrogen.

hysical Properties.—Nitrogen is a colorless, tasteless, odorless which is very slightly soluble in water; 100 volumes of the er dissolve 1.6 volumes of nitrogen. The density of nitrogen a chemical sources is 0.0012508, while that of the atmospheric nitrogen is 0.00125718. It was this difference in density of the gas from the two sources that led to the discovery of argon. The critical temperature of nitrogen is −146° and the critical pressure is 35 atmospheres. Its boiling-point is −195°. The liquid nitrogen is colorless and has a density, at its boiling-point, of 0.8103. At −210°, nitrogen freezes to a white solid.

The molecular wei is 28, and therefore, since its atomic weight is 14. is N_2.

Chemical Propert nost of the other elements, nitrogen ordinarily to be inactive. At higher temperatures, or un ice of the electric glow discharge it becomes fairl Vhen the gas is passed over strongly heated lithium, n, calcium, or boron, direct combination takes p formation of the nitrides of these elements, Li ${}_3N_2$, and BN. A mixture of powdered lime (calcium) and magnesium reacts so vigorously when heated in a current of nitrogen that the phenomena strongly resemble those of combustion of many substances in oxygen.

When nitrogen is mixed with either oxygen or hydrogen and heated, but little action takes place. When an electric spark is passed through either of these mixtures, some change occurs, but soon comes to an end since the reactions are reversible. In the case of nitrogen and oxygen, nitric oxide, NO, is first formed and this then combines with the excess of oxygen present to form nitrogen peroxide, NO_2. The nitrogen and hydrogen unite to form ammonia, NH_3. Nitrogen rendered active by the electric glow discharge will continue to glow for some time after the discharge has ceased, and will react with phosphorus, sodium, mercury, and with some compounds of carbon and hydrogen. In many respects it seems to be analogous to ozone, but is less stable than the latter.

Hydrogen Compounds of Nitrogen.—By far the most important of the compounds of hydrogen and nitrogen is ammonia, NH_3. Some idea of its importance may be gained from the fact that the yearly production of the compound and its salts is equal to 260,000 tons of ammonia. In addition to ammonia we have the less important compounds, hydrazine, N_2H_4, and hydronitric acid, HN_3.

Ammonia—Occurrence.—Ammonia is present in very small antities in the air and in all river and rain waters, both as combined ammonia and as ammonium nitrate, NH_4NO_3, and amonium nitrite, NH_4NO_2.

Preparation.—Ammonia may be prepared directly from the ements under the influence of an electric spark, or better, by ating a highly compressed mixture of nitrogen and hydrogen not over 750° in the presence of finely divided iron or uranium catalyzer.

An application of the law of mobile equilibrium to the equation r the reaction

$$N_2 + 3H_2 \rightleftarrows 2NH_3 + 50Kj$$

ows that since the volume of the ammonia is less than that f the elements, high pressure is favorable; while the evolution f heat indicates that ammonia will decompose with rising emperature, and therefore a low temperature will lead to a more omplete union of the elements.

This reaction is now being used for the synthesis of ammonia n a large scale. The pressure used is about 200 atmospheres nd one of the chief problems is to keep the apparatus gas-tight t the high pressure and temperature necessary.

Water acts upon nitrides forming ammonia and the hydroxide of the metal. The equation for the decomposition of magnesium nitride is given below:

$$Mg_3N_2 + 6H_2O = 3Mg(OH)_2 + 2NH_3$$

A somewhat analogous method consists in the formation of calcium cyanamide, $CaCN_2$, by the action of nitrogen upon calcium carbide, CaC_2, at fairly high temperatures:

$$CaC_2 + N_2 = CaCN_2 + C$$

Water decomposes this calcium cyanamide and yields calcium carbonate, $CaCO_3$, and ammonia,

$$CaCN_2 + 3H_2O = CaCO_3 + 2NH_3$$

These reactions are the basis of a thoroughly practical process for obtaining ammonia from the nitrogen of the air and are now being carried out on a very large scale.

Animal refuse including horns, hides, hair, feather when heated gives off a part of the nitrogen in the form monia. A solution of ammonia in water was formerly p in this way and was known as spirits o horn; a name that is sometimes used present day. Some ammonia is given o volcanoes and collects around them in t of ammonium chloride, NH_4Cl.

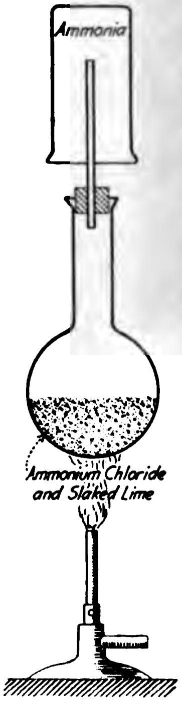


FIG. 33.

Coal contains upward of 2 per cent. o gen in combination with carbon, hydroge and when the coal is heated in the abs air, as in the manufacture of coal gas, some of the methods for making coke, a this nitrogen is given off in the form of nia. The gases are led through water dissolves the greater part of the ammo also many other substances. This "amm liquor" is then mixed with slaked lin heated. The ammonia is given off and a in dilute hydrochloric acid or sulfuri forming ammonium chloride, NH_4Cl, or nium sulfate, $(NH_4)_2SO_4$. The greater the ammonia of commerce is prepared fr in this way.

In the laboratory, ammonia is usua tained by gently heating a mixture of lime, $Ca(OH)_2$ and ammonium chlorid 33). Ammonium hydroxide is first form then decomposed into ammonia and water.

$$Ca(OH)_2 + 2NH_4Cl \rightleftarrows CaCl_2 + 2NH_4OH$$
$$NH_4OH \rightleftarrows NH_3 + H_2O$$

It may also be secured by heating a strong aqueous s of ammonia.

Ammonia cannot be dried by either sulfuric acid or c chloride, since it forms ammonium sulfate with the one compound, $CaCl_2{\cdot}8NH_3$, which strongly resembles a sa water of crystallization, with the other. Unslaked lime or potassium hydroxide is used to dry the ammonia.

rsical **Properties.**—Ammonia is a colorless gaseous sub- whose molecular weight is 17.034. It has a very strong cteristic odor which is familiar to everyone.

solubility in water is exceedingly great, one volume at temperature takes up 800 times its volume, or 0.6 of its ıt of ammonia. At zero degrees, water will dissolve even of the gas. In spite of the great solubility of ammonia, ll follows Henry's law approximately, especially at higher eratures.

e critical pressure of ammonia is 111 atmospheres, and its al temperature is 132°. It may therefore be liquefied by ure alone at ordinary temperatures. The boiling-point is 5°. It is a colorless, very mobile liquid which freezes to a , crystalline solid at $-77°$. The density of the liquid at oiling-point is 0.677. The liquid ammonia is a very good nt indeed for many substances, including a large number of When salts are dissolved in liquid ammonia, they are ciated very much as they are in water, though to a smaller e at any given concentration than when dissolved in water. ons travel faster in ammonia than in water, so that solutions lts in ammonia are often better conductors of electricity than ous solutions of the same salts.

uid ammonia is a very common article of commerce, com- ed in strong iron cylinders. The greater part of this is in plants for the **manufacture of ice** and for **cold storage.** se for such purposes depends upon the fact that, like all liquids, it absorbs a great amount of heat when it evapo- —the "heat of vaporization" as it is called. The ammonia not enter into the ice in any way, but is simply used as a er of heat from a lower to a higher temperature. Such a ss is not a spontaneous one, and can be brought about only he expenditure of work. The process may be briefly out- as follows:

e gaseous ammonia is compressed, generally by a steam n pump (Fig. 34), until it liquefies in a coil of iron pipes d by a stream of water. In liquefying, it gives out to the r the heat of condensation. The liquefied ammonia is then ed to escape into another coil of pipes, called the expansion in which it evaporates, thereby taking up from its surroundings the heat of evaporation. The gaseous ammonia p back from the expansion coil to the pump where it is re-c pressed and liquefied, giving up the heat absorbed in evaporat It then passes once more into the expansion coil and so is circulating through the system. The expansion coil is usu immersed in brine which is cooled by the evaporating ammoni temperatures below the freezing-point of water. Manufact ice is made by placing cans containing about 200 lb. of disti water in the brine and letting them stand until the water i frozen. The ice prepared in this way is very pure, and m superior to most natural ice for domestic purposes.

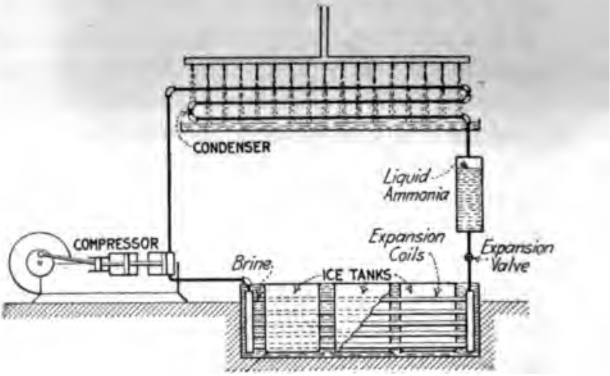


FIG. 34.

As was mentioned above, the ammonia simply serves to c the heat from a lower to a higher temperature at the expen the work done by the engine. Any other very easily vol liquid might be used instead of the ammonia, and several o have been so employed.

Chemical Properties of Ammonia.—When ammonia is he by electric sparks or otherwise, the reverse of the reaction f synthesis (see p. 193) takes place and it is largely decomp into its elements. The decomposition is more complete lower the pressure and the higher the temperature.

Ammonia will burn in oxygen but not in air. It burns a pale yellow flame forming water, nitrogen, ammonium ni NH_4NO_2, and ammonium nitrate, NH_4NO_3. In the presen a suitable catalyzer, platinum for example, ammonia will a moderate rate with oxygen of the air to form nitric acid. is is the basis of what is known as the Ostwald process of aking nitric acid.

When ammonia is passed over heated copper oxide or other sily reducible oxide, the metal, water, and nitrogen are usually btained.

When dry ammonia is passed over heated potassium or dium, hydrogen and potassium or sodium amide, KNH_2 or aNH₂ are formed:

$$2Na + 2NH_3 = 2NaNH_2 + H_2$$

The most prominent chemical property of ammonia is its bility to combine directly with acids for the formation of mmonium salts. For example, with hydrogen chloride, it rms dense white fumes of ammonium chloride:

$$NH_3 + HCl \rightleftarrows NH_4Cl$$

ith other acids the action is very similar as shown by the llowing equations:

$$2NH_3 + H_2SO_4 \rightleftarrows (NH_4)_2SO_4$$
$$NH_3 + HNO_3 = NH_4NO_3$$

ost of these salts, when heated to a sufficiently high temperaure, break down into ammonia and the acid from which they ere formed, just the reverse of the above process. Ammonium trate and nitrite are exceptions. The decomposition of amonium nitrite into nitrogen and water has already been given. he nitrate decomposes into nitrous oxide, N_2O, and water,

$$NH_4NO_3 = N_2O + 2H_2O$$

When ammonia dissolves in water, a part of it combines with e formation of ammonium hydroxide, NH_4OH,

$$NH_3 + H_2O \rightleftarrows NH_4OH$$

he reaction is reversible, and only a portion of the substances e present as hydroxide. At a temperature of −79°, ammonium ydroxide may be prepared as a white crystalline solid. Another ystalline compound of ammonia and water can be obtained at a low temperature. It has the composition $(NH_4)_2O$, and m be called ammonium oxide. Its freezing-point is −79°.

Ammonium hydroxide is a weak base and in normal soluti is dissociated to the extent of about 0.4 per cent. The ions a hydroxyl and ammonium, NH_4^+. This ammonium ion h many properties which are very similar to those of the potassiu ion.

Upon neutralizing ammonium hydroxide with acid and evapo ating the solution, salts are obtained which are identical wi those formed by direct union of the acids and ammonia. The salts like other salts, are highly dissociated when dissolved i water. With solutions of strong bases, they at once react, forming undissociated ammonium hydroxide which then breaks dow into the ammonia and water as was shown in the discussion of th preparation of ammonia. This reaction is used for the recognition of ammonium compounds. The ammonia is detected by it action on wet litmus, by the white fumes formed with hydrochloric acid, and even by its odor.

Ammonium salts, especially the sulfate and chloride, are mucl used as fertilizers to supply the necessary nitrogen for th growth of plants. The greater part of the 1,000,000 tons o ammonium salts which are annually produced is used as fertilizer

An excess of ammonia reacts with chlorine or bromine formin ammonium salts and nitrogen. The equation for the reactio with chlorine is given below; that for bromine is similar:

$$8NH_3 + 3Cl_2 = N_2 + 6NH_4Cl$$

Hypobromites and hypochlorites act upon ammonia in such way that all the nitrogen is set free in the gaseous state:

$$2NH_3 + 3NaBrO = 3NaBr + 3H_2O + N_2$$

Hydrazine.—Hydrazine, N_2H_4, is a colorless liquid which boi at 114° and freezes at 1°. It combines with water yielding hydrate, N_2H_6O, which is volatile without decomposition. will react with acids with the formation of salts. Two series such salts are known, N_2H_5A and $N_2H_6A_2$, in which A stands f any anion carrying one negative charge. Hydrazine is forme by the reduction of nitrogen compounds and is itself a very stro reducing agent.

Hydronitric Acid or Hydrazoic Acid.—The sodium salt of hydronitric acid or hydrazoic acid, as it is often called, may be prepared by the action of nitrous oxide, N_2O, upon sodium amide, $NaNH_2$:

$$NaNH_2 + N_2O = NaN_3 + H_2O$$

From this salt, the acid is prepared by distillation with dilute sulfuric acid. It is a colorless liquid with a strong and very disagreeable odor. It boils at 37° and explodes violently on contact with hot objects. The substance sometimes explodes at ordinary temperatures, thus making it very dangerous to handle.

It is a rather weak acid though somewhat stronger than acetic acid. Its salts resemble the chlorides except that the salts of the heavy metals are explosive and the difficultly soluble silver salt is soluble in the stronger acids, while the chloride is not.

Air.—Air is a mixture of a rather large number of gaseous substances and in addition always contains some floating particles of dust. The main gaseous constituents which are present in almost fixed proportions are nitrogen, oxygen and members of the argon group; in addition, it contains variable amounts of water vapor, carbon dioxide, and ammonia. In the neighborhood of cities and chemical works sulfur dioxide, hydrogen sulfide, hydrochloric acid and a few other gases are found. These may be regarded as impurities and neglected in the discussion of air.

The quantity of carbon dioxide varies from about 3 to 4 parts per 10,000 in the air of the country to 6 to 7 parts in the cities and in badly ventilated rooms may run up to 50 parts. This carbon dioxide is formed during the burning or decay of any carbonaceous materials, and is also given off during the breathing of animals. It is however taken up by green plants, and with the aid of the energy absorbed from the light of the sun, is utilized in building up the various plant tissues, oxygen being set free at the same time. This tends to keep the carbon dioxide content of the air approximately constant.

Composition of the Air.—The quantity of water vapor present in the air is so variable that no definite statement concerning it can be made, but the composition of dry air is shown in the following table:

Dry Air contains:

Per cubic meter	Per kilogram
781.3 liters nitrogen	755.14 grm.
209.9 liters oxygen	231.47 grm.
9.4 liters argon, etc	12.92 grm.
0.3 liters carbon dioxide	0.46 grm.
0.1 liters hydrogen	0.01 grm.

The term argon, etc., includes , helium, neon, krypton and xenon.

In spite of the many factors w tend to change the composition of the air, the winds produ uch a thorough mixing that its composition remains practic fixed, although measurable variations do occur.

The density of dry air is 0.0 under standard conditions. In contact with water, each gas ssolves in proportion corresponding to its solubility and its partial pressure as described by Henry's law. The solubility of oxygen is so much greater than that of nitrogen that in spite of its smaller partial pressure relatively more oxygen than nitrogen dissolves.

Liquid Air.—The critical temperature of air is −140° and its critical pressure about 39 atmospheres. Liquid air boils from −194° to −185° according to its composition, and when first prepared contains from 28 to 50 per cent. of oxygen. As it stands, the nitrogen (boiling-point −195°) tends to pass off first and leaves the oxygen (boiling-point −182.5°) behind. This is made the basis of very practical methods for obtaining both oxygen and nitrogen from the air sufficiently pure for many commercial purposes. Liquid nitrogen has a smaller density than that of water, while the reverse is the case with liquid oxygen. Liquid air when freshly prepared is specifically lighter than water, but on partial evaporation becomes heavier. The color also changes from practically colorless to the blue of liquid oxygen.

To liquefy air it is first partially freed from carbon dioxide by slaked lime, and then compressed to 150 to 200 atmospheres. A great deal of heat is developed in this process so the gas is cooled to ordinary temperatures by water in the jackets around the compressor (Fig. 35), and by passing it through a coil surrounded by water. The greater part of the water vapor in the air condenses at this high pressure and the remainder together th the rest of the carbon dioxide is removed by potassium droxide. The purified highly compressed air then enters the uefier at the temperature of the room. The liquefier consists a coil of very small copper tubing carrying at its lower end a lve for controlling the flow of the air. The whole is inclosed a metal jacket and thoroughly insulated from its surroundings wool. Through the copper tube, the air flows in a continuous eam and as it escapes from the valve at the lower end of the

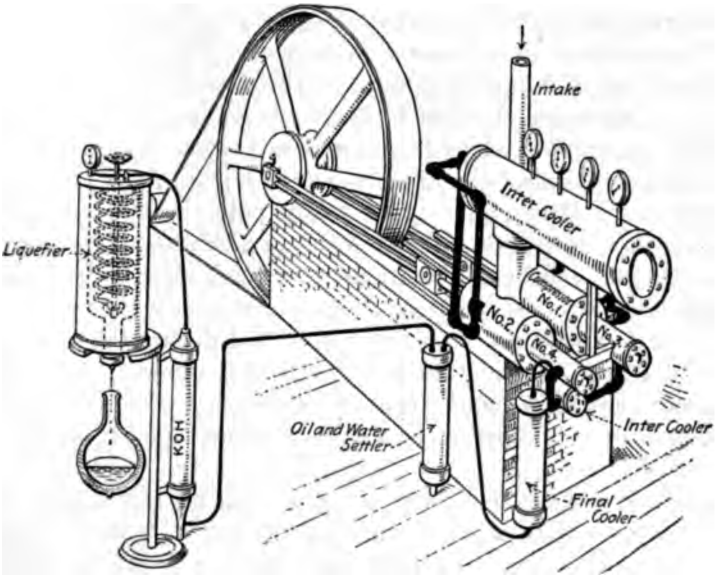


FIG. 35.

coil, it becomes somewhat cooler. By the construction of the apparatus, this cooled air is compelled to pass up over the coil thereby cooling it together with the oncoming air which reaches the valve at a lower temperature than the first of the stream, and in expanding becomes still cooler and in turn lowers the temperaure of the coil. This process goes on until a few minutes after tarting the machine the temperature has been so far lowered hat about 5 per cent. of the air issuing from the expansion valve liquefied. The rest is returned to the machine, recompressed nd sent around the cycle once more. In large plants part of the oling is accomplished with carbon dioxide and ethylene.

The liquid air must not be corked up and will evaporate rapidly as it can get the necessary heat, so after it is obtained is preserved in double-walled vacuum-jacketed vessels which a usually coated on the inside of the walls with silver. Su vessels are very good heat insulators indeed.

Liquid air on account of its low boiling-point is an exceeding useful substance for investigations at low temperatures.

Experiments.—Many interesting and striking experimen may be performed with liquid air. These depend essentiall upon two properties; first that it has a very low boiling-poin and second that it is a source of oxygen. When cooled to th temperature of liquid air, most of the familiar gases such a chlorine, hydrogen chloride, hydrogen bromide, ammonia, sulfu dioxide, methane and hydrogen sulfide become odorless solids Liquids such as alcohol and kerosene freeze, and rubber become as brittle as glass and may be easily pulverized in a morta Metals such as copper and steel become a third stronger towar a steady pull, but break readily under a quick blow. Crystallin metals, on the other hand, are distinctly weaker in every way a this low temperature. The heat absorbed during the evaporation of 1 grm. of liquid air plus the heat required to warm th gaseous air to 0° is about 80 cal., so the cooling effect of a poun of liquid air in a refrigerator would be about equal to that of pound of ice.

When liquid air boils, the nitrogen goes off faster than th oxygen, and after a time almost pure liquid oxygen is lef This furnishes oxygen of such concentration that charcoal steel will burn with exceeding brilliancy in the liquid. Cotto or charcoal wet with just the proper amount of oxygen to complete the combustion will explode when set off with a mercu fulminate cap with the violence of an equal weight of dynamit Aluminum powder made into a paste with liquid oxygen w burn with a blinding flash upon contact with a flame, and th temperature of the mass is changed in a small fraction of second from 183° below to something like 3,000° above zero.

Air is a Mixture.—That air is a homogeneous mixture and n a chemical compound is shown by several arguments.

1. Nitrogen and oxygen may be mixed in the proportion which they are present in the air, and no heat effect will resu

) changes in volume, nor any other evidence of chemical transrmation and yet the mixture behaves like air in every respect.

2. The composition of the air varies while that of a compound perfectly fixed.

3. Relatively more oxygen than nitrogen is dissolved by ater, while a compound dissolves as a whole, without any ıange in the proportions of the components.

4. The properties of the air are a mean of the properties of its ›mponents, which would not be true if it were a compound.

5. The separation of the gases by liquefaction and fractional istillation indicates a mixture.

Air and Life.—Oxygen is absolutely indispensable for the connuance of all forms of animal life. The purely aquatic forms get heir oxygen from air dissolved in the water, while the rest breathe he air directly. We, for example, take in about half a liter of ir at each breath, and remove from this about 5 per cent. of the xygen, giving to it about 3.7 per cent. of carbon dioxide. The itrogen is unchanged. The oxygen taken up in the lungs argely enters into a loose combination with a substance called ıemoglobin in the red corpuscles of the blood and is carried to ll parts of the body, gradually oxidizing the various body ubstances, chiefly to carbon dioxide, water, and fairly simple ompounds of carbon, nitrogen, hydrogen, and oxygen. The arbon dioxide is largely given up by the blood to the air upon ts return to the lungs. The oxidation of these substances is the ource of the body heat, and of the energy which we spend as rork.

Oxides and Oxyacids of Nitrogen.—There are five oxides of itrogen. Three of these are anhydrides of acids. The names nd formulas of these oxides are given in the following table with he names and formulas of the acids opposite their anhydrides.

itrous oxide or hyponitrous anhydride...... N_2O	Hyponitrous acid....... $H_2N_2O_2$
itric oxide............ NO	....
itrogen trioxide or nitrous anhydride...... N_2O_3	Nitrous acid............ HNO_2
itrogen peroxide....... NO_2 or N_2O_4	....
itrogen pentoxide or nitric anhydride....... N_2O_5	Nitric acid............. HNO_3

Nitric Acid.—Nitric acid, the most important of the oxyaci does not occur free in nature, but its salts are present in fertile soils. Potassium nitrate, KNO_3, has been known centuries under the name of saltpeter. The sodium salt, NaN occurs in great deposits in the desert regions of Chile, and he is called Chile saltpeter. Enormous quantities of this extracted and shipped all ıe world for use in prepari other nitrogen compounds, anc a fertilizer.

Under the influence of el l discharges nitrogen, oxyg and water will combine for the mation of nitric acid, and th together with the am f air, is doubtless the source the ammonium nitrat n rain water.

Certain forms of ria e able to convert ammonia a nitrogenous organic s ces to nitric acid the latter th reacts with the calcium carbor e of the soil to form calciu nitrate, $Ca(NO_3)_2$.

Nitric acid is prepared by the first general method by distilli sodium nitrate with sulfuric acid in cast-iron retorts. Enou sulfuric acid is used to make the sodium acid sulfate which either sold as such or heated with sodium chloride to make hyd chloric acid and the neutral sulfate.

$$NaNO_3 + H_2SO_4 = NaHSO_4 + HNO_3$$

Pure nitric acid is a colorless liquid having a density of 1. at 15°. It boils at 86°. It gradually decomposes, especia under the influence of light into oxygen, water, and oxides nitrogen, which color the acid yellow. The addition of wa makes the acid much more stable. The conductivity of the p solution is much greater than that of the pure acid which indica that the water has changed the acid into ions. This may acco for the increased stability. As water is added to the acid, boiling-point gradually rises until when a 68 per cent. acid formed, the boiling-point reaches a maximum at 120°. The lations here are very similar to those between hydrochloric a and water.

Chemical Properties of Nitric Acid.—The chief chemical pr erties of nitric acid depend upon the fact that it is both a str acid and very powerful oxidizing agent.

As an acid it is as strong as any, being as highly dissocia into its ions at any given dilution as hydrochloric acid. Consequently it is able to do anything that depends upon the concentration of the hydrogen ions, which any other acid can do.

As will be recalled, the ordinary reaction between an acid and a metal whereby the metal is dissolved and hydrogen is liberated is regarded as taking place between the metal and the hydrogen ion, and as consisting of the oxidation of the metal to its ion and the reduction of the hydrogen ion to the free element. For example, in that between zinc and hydrochloric acid, the chlorine ion is considered to take no part, the entire reaction being between the zinc and the hydrogen ion,

$$Zn + 2H^+ + 2Cl^- \rightleftarrows Zn^{++} + 2Cl^- + H_2$$

or, leaving out the idle chlorine ion,

$$Zn + 2H^+ \rightleftarrows Zn^{++} + H_2$$

Nitric acid being a strong acid its hydrogen ion is as well able to oxidize metals as hydrochloric and in addition, because of its being a nitrate, nitric acid is able to oxidize and dissolve copper, mercury, and silver which hydrochloric cannot do. It cannot be too strongly emphasized that in the case of these last-mentioned metals hydrogen is *not* given off, but in its place nitric oxide appears. The nitrogen in nitric acid, in which it has a valence of 5 positive, has a great tendency to pass into nitric oxide in which it has a valence of 2 positive, and in so doing exerts a very powerful oxidizing action, much more so than the hydrogen ion and consequently is able to oxidize copper, mercury and silver which hydrogen as ion cannot do. The equation for the action on copper is as follows:

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 2NO + 4H_2O.$$

In the discussion of the halogens, it was pointed out that concentrated sulfuric acid is a rather powerful oxidizing agent. It is much stronger than the hydrogen ion and will oxidize copper, mercury, and silver to their ions. As with nitric acid, hydrogen gas is not evolved, but an oxide, sulfur dioxide in this case, is given off. Here again we have a change in valence, for the sulfur in sulfuric acid is 6 positive and in sulfur dioxide 4 positive. The equation for the reaction between sulfuric acid and copper is:

$$Cu + 2H_2SO_4 = CuSO_4 + SO_2 + 2H_2O$$

As has been pointed out, a change of valence such as we have just mentioned is an essential accompaniment of oxidation.

Gold and platinum are lized by nitric acid in the absence of chlorine as ion, efore this acid is used in the refining of these metals to the silver, etc., with which they may be alloyed. Becau the vigor of its action on metals, nitric acid was form ed aqua fortis.

In addition to its use as ind above, nitric acid is largely employed in the laboratory an the manufacture of nitrates, dyestuffs, sulfuric acid, nitrogly e, guncotton, etc.

Aqua Regia.—Aqua regia is a mixture of nitric and hydrochloric acids, and is capable of attacking gold and platinum, metals which do not dissolve in either of these acids alone. The action is not due to aqua regia's being primarily a stronger oxidizing agent than the nitric acid but to the fact that the chlorides of gold and platinum are much more stable than their nitrates and in aqua regia, the chlorides of the metals may be formed. This increased stability of the chloride over the nitrate materially assists in the oxidation of the metals and is enough to enable the nitrate to do the work, but not sufficient to cause the hydrogen ion from hydrochloric acid to oxidize the gold or platinum.

Aqua regia received its name long ago when the alchemists found that it was a solvent for gold which they considered to be the king of metals.

When aqua regia is heated alone, it gives off chlorine and compounds of nitrogen, oxygen, and chlorine; one of these is nitrosyl chloride, $NOCl$.

Nitrates.—Nitric acid, as is indicated by its formula, is a monobasic acid and yields only one series of salts, the nitrates. These are formed by the action of the acid upon the metals or bases.

These salts are all readily soluble in water. The nitrates are decomposed rather easily at elevated temperatures, generally giving oxygen, oxides of nitrogen, and the oxide of the metal Most of the applications of nitrates depend upon their action as oxidizing agents. When heated with charcoal they often ıate. Potassium nitrate, charcoal, and sulfur in the ɜr proportions constitute gunpowder.

tro Compounds.—Very concentrated nitric acid acts upon ›ounds of carbon and hydrogen forming nitro-compounds water. For example, nitric acid and benzene, C_6H_6, react he formation of nitrobenzene, $C_6H_5NO_2$, and water.

$$C_6H_6 + HNO_3 = C_6H_5NO_2 + H_2O$$

group NO_2 is known as the nitro group. The water formed ıe reaction is detrimental, so concentrated sulfuric acid is d with the nitric acid to take up this water.

cohols (carbon, hydrogen and oxygen compounds containing oxyl) react with nitric and sulfuric acids for the formation ımpounds which in their formulas are similar to nitrates, but h are not salts. Glyceryl nitrate or nitroglycerine, C_3H_5- $_3)_3$, is formed by the action of this mixture of acids upon an ıol called glycerine, $C_3H_5(OH)_3$:

$$C_3H_5(OH)_3 + 3HNO_3 = C_3H_5(NO_3)_3 + 3H_2O$$

itrogen Pentoxide.—Nitrogen pentoxide N_2O_5 is a colorless, ile, very volatile liquid which soon passes over into a white talline solid, melting at 30°. It is made by distilling a ure of phosphorus pentoxide and nitric acid. It is the ʼdride of nitric acid.

itric Oxide.—Nitric oxide, NO, is formed by the action of ɜwhat dilute nitric acid, sp. gr. 1.2, upon copper, as shown ıe following equation:

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 2NO + 4H_2O$$

gas so obtained is never pure, since it always contains some ›us oxide, N_2O, and often nitrogen.

he pure oxide may be obtained by adding nitric acid to a ng solution of ferrous sulfate, $FeSO_4$, in dilute sulfuric acid. equation is as follows:

$$eSO_4 + 3H_2SO_4 + 2HNO_3 = 3Fe_2(SO_4)_3 + 2NO + 4H_2O$$

ferrous sulfate is oxidized to ferric sulfate, $Fe_2(SO_4)_3$, and nitric acid reduced to nitric oxide.

roperties of Nitric Oxide.—Nitric oxide is a colo se molecular weight is 30 corresponding to its for

It is only slightly soluble in water. The critical temperature of the gas is $-93°$, and its boiling-point is $-150.2°$. So it is more like the so-called permanent gases, oxygen, hydrogen, etc., than most of the gaseous substances which we have been discussing.

Nitric oxide is the most stable toward heat of the oxides of nitrogen. Even when heated to a temperature of 2,000° only about 1 per cent. of it is [illegible]d. In fact it is formed from its elements at very high [illegible]res, and may be obtained by passing the electric spark thro[illegible]r. This is made the basis of a successful method for the p[illegible]ion of nitric acid and nitrates on a commercial scale as will [illegible]lained later.

Briskly burning wood [illegible]r pho[illegible]us continues to burn in nitric oxide. The flame is a[illegible]ht as when the combustion takes place in oxygen. [illegible] ot[illegible] burning substances, for example a candle or sulfur, are extinguished. Since the heat of formation of nitric oxide is -90 Kj. considerable heat is evolved in its decomposition, and a given quantity of a substance like phosphorus burning in NO will liberate more heat than if it had burned in oxygen.

Nitric oxide combines directly with oxygen at ordinary temperatures, forming the reddish-brown nitrogen peroxide, NO_2:

$$2NO + O_2 = 2NO_2$$

This nitrogen peroxide is at once formed whenever the nitric oxide comes in contact with the air, consequently it is impossible to say anything about the odor of nitric oxide.

Nitric oxide is soluble in solutions of ferrous salts with the production of a dark brown solution containing $FeNO^{++}$. From this solution the oxide is driven out by heating to the boiling-point. In this way pure NO may easily be obtained from mixtures with other gases, since the latter are either not absorbed in the first place or are retained when the solution is boiled.

The formation of this dark colored solution may be utilized as a test for nitric acid, a nitrate, or in general any oxygen compound of nitrogen higher than nitric oxide. The equation for the reduction of nitric acid to nitric oxide is given on page 207.

Nitrogen Peroxide.—Nitrogen peroxide as has already been mentioned is formed by the direct union of oxygen and nit oxide. It may also be prepared by heating certain nitrat ead nitrate, for example, decomposes to give nitrogen peroxide, xygen, and lead oxide, as shown by the following equation:

$$2Pb(NO_3)_2 = 4NO_2 + O_2 + 2PbO$$

It condenses to a yellowish-red liquid which boils at 22° and at low temperatures freezes to an almost colorless solid, melting at −12°.

The molecular weight of the gaseous compound varies with the conditions of temperature and pressure under which it is determined. At low temperatures and rather high pressures it is early 92, corresponding to a formula for the compound of N_2O_4. s the temperature is raised and the pressure diminished, the olecular weight gradually falls until it reaches a limit of 46, orresponding to the formula NO_2. This change from one rm to the other is accompanied by a marked change in color. t rather low temperatures the gas has a yellow-brown color, s the temperature is rasied it becomes darker and darker ntil at 154° it has reached such a deep black-red that it is almost paque, even in thin layers.

When nitrogen peroxide is heated above 154°, it gradually oses its dark color as the temperature rises, and finally becomes olorless. This color change is due to the transformation of NO_2 into NO and oxygen.

$$2NO_2 \rightleftarrows 2NO + O_2$$

his decomposition becomes practically complete at 620°.

Nitrogen peroxide reacts with water to form nitric acid and NO,

$$3NO_2 + H_2O = 2HNO_3 + NO$$

n the presence of air, NO will pass into NO_2, which in turn will orm more nitric acid. So the reaction of NO_2, air, and water will ltimately yield the whole of the nitrogen in the form of nitric cid.

$$4NO_2 + O_2 + 2H_2O = 4HNO_3$$

Nitric Acid from the Air.—When air is passed through an lectric arc, its temperature becomes extremely high, and a mall quantity of nitrogen and oxygen unite to form nitric oxide. When this has cooled sufficiently, it unites with oxygen nitrogen peroxide; which then will react with water and oxy as shown in the preceding section to form nitric acid. 1 process has recently become of great importance and is car out at many places, but one of the largest plants is at Notodc Norway. Here the arc is formed by a high potential alternat current between copper electrodes which are placed at ri angles to the poles of a powerful electromagnet. Under th conditions the arc is forced to move rapidly alternately up a down according to the direction of the current so that it appe to form a flat disc of electric flame (Fig. 36) through which

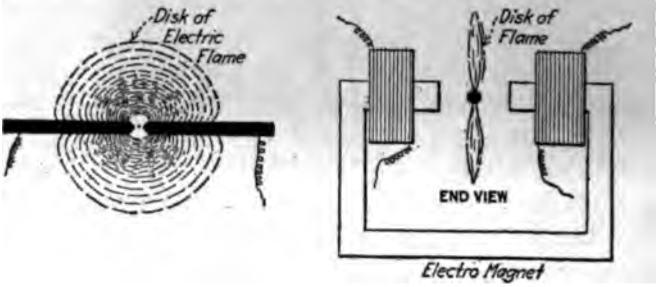


Fig. 36.

air passes. The oxides of nitrogen formed are taken up water in towers similar to the Glover or Gay Lussac towers, the nitric acid is either concentrated and used in this form is converted into calcium nitrate by letting it act upon sla lime.

The calcium nitrate is a good fertilizer and is put on the ma at a low enough price to compete with the Chile saltpeter.

Nitrites.—When potassium or sodium nitrates are hea especially in the presence of a reducing agent like lead, they one atomic weight of oxygen per mole and are changed i nitrites,

$$NaNO_3 + Pb = NaNO_2 + PbO$$

When an acid is added to a strong solution of a nitrite, nitrous acid formed breaks up immediately into water and nit anhydride, N_2O_3; but the latter at once almost completely composes into nitrogen peroxide and nitric oxide,

$$2HNO_2 \rightleftarrows H_2O + N_2O_3$$
$$N_2O_3 \rightleftarrows NO_2 + NO$$

this way a nitrite is easily distinguished from a nitrate, since e nitrogen peroxide is so highly colored.

Nitrous acid oxidizes good reducing agents while it is itself idized by strong oxidizing agents. For example, it oxidizes HI, d reduces potassium permanganate, $KMnO_4$. The nitrites e largely used in the manufacture of organic dyes.

Nitrous Anhydride.—Besides the method just given for the rmation of nitric oxide and the peroxide in the preparation of trous anhydride, this same mixture may be obtained by heating senic trioxide, As_2O_3, with nitric acid having a density of 1.30 1.35. The arsenic trioxide is oxidized to the pentoxide, As_2O_5, d the nitric acid reduced to nitrous which at once breaks down to water and the mixture of the two oxides. This mixture of e two oxides may be condensed by a freezing mixture to a dark-ue liquid which boils at 3.5°. If the liquid is completely dried, may then be vaporized without dissociating. So dry nitrous hydride, N_2O_3, can exist while the moist compound cannot.

Hyponitrites and Hyponitrous Acid.—Sodium hyponitrite, $a_2N_2O_2$, may be made by reducing sodium nitrite with sodium malgam. From this hyponitrous acid may be made. It is a lid which decomposes irreversibly into water and nitrous oxide $_2O$; hence the latter is often called hyponitrous anhydride.

Nitrous Oxide.—Nitrous oxide is readily prepared by heating mmonium nitrate, which decomposes into this substance and ater,

$$NH_4NO_3 = N_2O + 2H_2O$$

t is a colorless gaseous substance which has a faint odor and is airly soluble in cold water. At room temperatures, water will issolve about its own volume of the oxide. Its critical pressure s 75 atmospheres and its critical temperature + 36°; so it is asily liquefied by pressure alone at ordinary temperatures. The boiling-point is −90°. The molecular weight of the oxide is 44 and its formula N_2O.

Nitrous oxide parts with its oxygen rather more readily than nitric oxide so that it will not only continue to support combustion of brightly burning wood as nitric oxide does, but will even cause a glowing splinter to burst into flame. Briskly burning phosphorous and sulfur will also continue to burn vigorously in nitrous oxide. In all cases, oxides are formed and nitrogen set free.

Nitrous oxide when breathed produces insensibility, and hence it is used as an anesthetic. The body does not decompose the nitrous oxide in such a way as to utilize the oxygen, so when it is to be breathed for any length of time, it is mixed with the amount of oxygen required [illegible]upport life. For use as an anesthetic, very pure nitrous [illegible]de is put on the market in the liquid form in strong iron [illegible]ders.

Nitrogen and Life.—Compou[illegible]ds of nitrogen are always present in all living organisms. They are especially abundant in the brain, nerves, and muscles, or, in short, in the tissues which seem to be most closely connected with the vital functions. Most organisms are entirely un[illegible] to make any use of the great store of free nitrogen in the air, but must get it from ready formed compounds. The plants as a rule get theirs from the nitrates, etc., which are present in the soil, while the animals obtain the compounds directly or indirectly from the plants.

Upon the decay of these organisms a portion of the nitrogen is liberated in the free state. From this it would seem that the supply of available nitrogen compounds must be continually decreasing. However, there are two important natural processes going on which tend to keep up the supply of nitrogen compounds available for plants. The first of these is the formation of nitric oxide during the passage of lightning through the air. The oxide is then transformed into nitric acid by the action of oxygen and water. This combines with the ammonia of the air to form ammonium nitrate which is carried by the rain into the soil. The second process takes place with the aid of certain forms of bacteria. Some forms are free in the soil, but the most efficient live in tubercules on the roots of leguminous plants such as clover, peas, alfalfa, etc. These bacteria have the power to transform the free nitrogen of the air into compounds which are closely related to the albumins, and which may be easily assimilated by the plant. Such plants will grow and produce abundant crops, and yet leave in the soil an increased amount of nitrogen compounds. This, then, is the explanation for the well-known fact that the fertility of certain soils may be restored by growing upon them these leguminous plants. In the older parts of the country, is the custom of farmers to raise a crop of such plants on h portion of cultivated land about once in three years. The mers of the West will doubtless have to adopt this same custom the course of time, if they continue to remove everything from e land and return nothing to it, and to burn the stalks and raw as so many do at present.

In addition, as has been mentioned, the compounds of ammonia ich are obtained in the manufacture of coal gas and coke, as ll as the calcium cyanamide and calcium nitrate which are ng made from the nitrogen of the air are available as fertilizers. there seems to be no danger that the earth will lose its fertility ause of lack of combined nitrogen.

CHAPTER XV

PHOSPHORUS

General.—Phosphorus belongs to a group of elements of which nitrogen is the member with the smallest atomic weight. Just as fluorine, the first member of the halogens, has some points of resemblance to chlorine but many of difference, so the nitrogen compounds have at least a formal similarity to those of phosphorus, but show many marked differences. *It might be said that the root of the differences lies in the fact that the more highly oxidized compounds of nitrogen are unstable and tend to go to the less highly oxidized, while just the reverse is the case with phosphorus.* Phosphorus, however, differs radically from nitrogen in that the element itself is extremely active chemically. When exposed to the air even at ordinary temperatures it is slowly oxidized, at the same time emitting light. It was on account of this property that phosphorus received its name, which means light bearer.

Occurrence.—Phosphorus does not occur free in nature, but is found widely distributed chiefly in the form of phosphates. The most important naturally occurring phosphate is that of calcium, $Ca_3(PO_4)_2$, which is found in most soils. It constitutes a large part of the bones and teeth of animals. Great beds of calcium phosphate which have been formed in part at least from the fossil bones of animals are found in Florida and Tunis. Enormous beds, probably the largest in the world, of phosphate rock exist in Utah, Montana, Wyoming, and Idaho. A very partial survey of the field has located 2,500,000,000 tons of rock averaging 70 per cent. calcium phosphate. Another mineral which is closely related to calcium phosphate is apatite, $Ca_5F(PO_4)_3$. This is a component of many rocks and is found in large quantities i Canada. The importance of these compounds of phosphoru may be realized when it is known that phosphorus like nitroge is an absolutely essential component of all living organisms, an hat soluble compounds of this element must be present in a soil in order that it may be fertile. In nearly all of the older agricultural countries, artificial manures containing phosphoric acid must be applied to the land. The world mines about 5,000,000 tons of phosphate rock per year.

Preparation of Phosphorus.—The easiest method of preparing phosphorus involves the heating of a mixture of calcium phosphate, sand (silicon dioxide), SiO_2, and carbon to a very high temperature in an electric furnace (Fig. 37). Calcium silicate, $CaSiO_3$, carbon monoxide, CO, and phosphorus are formed.

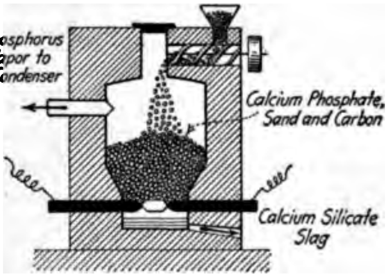

Phosphorus Vapor to Condenser
Calcium Phosphate, Sand and Carbon
Calcium Silicate Slag

FIG. 37.

The carbon monoxide and phosphorus pass out of the furnace in the gaseous state, the phosphorus being condensed under water. The calcium silicate is liquid at the temperature of the reaction and is drawn off from the furnace from time to time. The whole process may be made continuous by feeding in the reaction mixture as rapidly as it is used up. The equation is:

$$2Ca_3(PO_4)_2 + 6SiO_2 + 10C = 6CaSiO_3 + 10CO + P_4$$

The Allotropic Modifications of Phosphorus.—The element phosphorus exists in two different modifications which are so very unlike that it is hard to believe that they are composed of the same element. One of these is called ordinary, yellow, or sometimes white phosphorus; the other is known as red phosphorus. In addition there is a black variety which is much like the red.

Ordinary phosphorus is prepared by the method described above and is a slightly yellowish almost colorless wax-like solid. It melts at +44° and boils at 270°. It is readily soluble in carbon disulfide and some other organic solvents, but is insoluble in water, under which it is always preserved. its solution in carbon disulfide, crystals of phosphorus m easily obtained.

When exposed to the air, this form of phosphorus is oxidized with the formation of phosphorus trioxide, P_4O_6, a the same time shines so that it may easily be seen in the In a limited amount of air, the luminosity will continue unt last detectable trace of oxygen has been used up. The perature of the phosphorus is but little higher than its roundings, so a part of the chemical energy of the change be converted directly into light. The fumes given off h

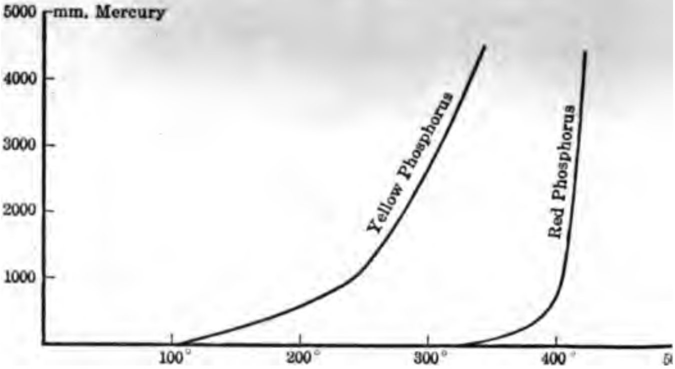


Fig. 38.

strong garlic-like smell and their continual inhalation duces a very serious disease in which the bones of the jaw Matchmakers are particularly liable to this trouble. element itself is very poisonous, a tenth of a gram being a dose. During the slow oxidation of the phosphorus, a part oxygen of the air is changed into ozone. If the temperat phosphorus exposed to air is gradually raised, the oxi goes on more and more rapidly until at about 45° it passe rapid combustion.

The molecular weight of phosphorus, both as vapor and lution is 124, and, since its atomic weight is 31.04, the fo is P_4.

Red phosphorus is very different from the ordinary form. It a dull red crystalline powder and may be obtained by heating e yellow variety to 250° in the absence of air. The trans- mation is catalyzed by iodine so that in the presence of a ace of this substance the transition takes place very rapidly deed at 200°. Light also hastens the change, and sticks of osphorus which have been exposed at ordinary temperatures the action of light are covered with a thin layer of red phos- orus.

Red phosphorus does not melt but passes directly into the apor which is identical with that of yellow phosphorus, and ields the latter modification when it is rapidly cooled. In fact, is only by converting the red phosphorus into the vapor and ondensing the latter that the change from the red into the ther modification can be made.

Red phosphorus is not poisonous, is not soluble in carbon disul- de, does not oxidize in the air at ordinary temperatures, nor ike fire until heated to about 260°. It is, then, very different om the ordinary phosphorus, and yet the two modifications can e converted the one into the other without any change in weight.

The yellow modification is at all ordinary temperatures un- table with respect to the red. In accord with this is the fact hat yellow phosphorus is more soluble than red and has the reater vapor pressure as shown by the curves given in Fig. 36. he vapor pressure curves do not intersect so there is no transi- ion point within the range 100°–400°, but there is a little evidence hat a transition point may exist at −77°.

When yellow phosphorus is heated to 200° under a pressure of bout 4,000 atmospheres it is changed into a more dense variety hich because of its color is called **black phosphorus.** This is hemically much like the red modification.

Hydrogen Compounds of Phosphorus.—Hydrogen and phos- horus form three compounds, phosphine, PH_3, liquid hydrogen hosphide, P_2H_4, and solid hydrogen phosphide, P_4H_2. Phos- hine is similar to ammonia in its formula and is slightly like it n its properties.

Phosphine may be readily prepared by dropping pieces of cal- ium phosphide, Ca_3P_2 (Fig. 39), in water.

$$Ca_3P_2 + 6H_2O = 3Ca(OH)_2 + 2PH_3$$

The action is very much like that between magnesium nitride and water with the formation of ammonia. The addition of a little acid facilitates the reaction by rapidly dissolving the calcium hydroxide. The phosphine prepared in this way is spontaneously inflammable.

As each bubble of phosphine rises to the surface of the water it catches fire with a little explosion and burns to phosphoric acid which forms a beautiful smoke ring. Pure phosphine is not spontaneously inflammable. The compound prepared as described above contains small quantities of the vapor of the liquid hydrogen phosphide, and it is to this that it owes the property of catching fire on contact with the air.

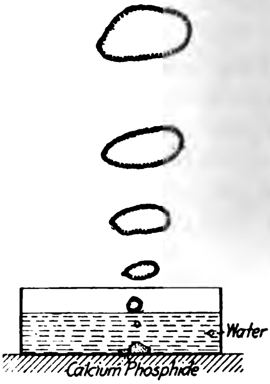


FIG. 39.

Calcium phosphide has found application in connection with life buoys to indicate their position at night when they are thrown into the water.

The phosphine may be so far purified from the liquid compound by passing it through a tube surrounded by a freezing mixture that it will not take fire on contact with the air.

Phosphine is a colorless gaseous substance which boils at −86°, smells like decayed fish and is very poisonous. At high temperatures it is decomposed into its elements. It resembles ammonia in its formula and because it combines directly with the hydrohalogen acids to form phosphonium salts. It differs from ammonia in that it is scarcely at all soluble in water and does not form a basic compound with this substance nor does it combine with the oxyacids to form salts.

Phosphonium Compounds.—Phosphonium iodide is the most stable of these compounds and is easily formed by bringing together at ordinary temperatures and pressures phosphine and hydrogen iodide,

$$PH_3 + HI = PH_4I$$

It forms beautiful large transparent quadratic crystals which sublime at 62°. In the vapor state, it is very largely decomposed to phosphine and the acid, just as ammonium salts are decom-sed into ammonia and the acid. It is a powerful reducing ent and finds use as such in the laboratory.

Phosphonium bromide is very similar to the iodide, and is repared from hydrogen bromide and phosphine at ordinary mperatures and pressures. It sublimes at 38°.

Phosphonium chloride cannot be prepared by bringing hydro-hloric acid and phosphine together at ordinary temperatures nd pressures. At $-35°$ it can be obtained at ordinary pressures, ut requires a total pressure of at least 18 atmospheres at 14° to roduce it or to keep it from decomposing into its components. Phosphonium compounds are decomposed by water into phosphine and the acid. From this we gather that the phosphonium ion, PH_4^+, is not stable.

Liquid Hydrogen Phosphide.—Liquid hydrogen phosphide boils at 57°. The vapor is spontaneously inflammable. Its analysis and molecular weight indicate that the formula is P_2H_4.

Halogen Compounds of Phosphorus.—Each of the halogens will combine directly with phosphorus forming fairly stable compounds.

Chlorine, bromine and iodine form trihalides, PCl_3 for example, which are all liquids. Fluorine, chlorine and bromine form penta compounds, PCl_5 for instance; with the exception of the fluoride which is gaseous, these are solids.

Each of these compounds is decomposed by water with the formation of an oxyacid of phosphorus and the hydroacid of the halogen. It will be recalled that this property was made use of in the preparation of hydriodic and hydrobromic acids. The chlorine compounds are rather more important than the others and will be described in some detail.

Phosphorus trichloride, PCl_3, is formed by passing chlorine over phosphorus contained in a retort to which is connected a receiver. The combination takes place with the evolution of so much heat that the greater part of the trichloride formed distills over and condenses to a colorless liquid in the receiver. It boils at 76° and has a density of 1.6. It reacts with water and other compounds containing oxygen and hydrogen to form phosphorous acid and hydrogen chloride. Because of this it fumes when in contact with moist air.

Phosphorus pentachloride, PCl_5, is prepared by the action of an excess of chlorine upon the trichloride. It is a pale yellowish-green solid which when heated under atmospheric pressure does not melt, but passes directly into the vapor without going through the liquid state. This is due to the fact that the temperature at which the vapor pressure of the solid is equal to the pressure of the air is lower than its melting point. We might say that its boiling-point is lower than its freezing-point. When the vapors are cooled they pass directly back to the solid state. That kind of distillation in which the solid passes directly into the vapor and reappears in the solid state upon cooling without the liquid modification coming in as an intermediate step is called sublimation. By heating the pentachloride under presssure, the boiling-point may be so raised that it lies above the melting-point which is 166°. In the vapor state, phosphorus pentachloride, PCl_5, is partially decomposed into chlorine and the trichloride.

Phosphorus pentachloride fumes strongly in contact with air and has a very irritating action on the mucous membrane. It rapidly reacts with water, forming phosphoric acid, H_3PO_4, and hydrogen chloride.

Oxygen Compounds of Phosphorus.—The oxides of phosphorus are the tetroxide, P_2O_4, and trioxide, P_2O_3, or P_4O_6, and the pentoxide, P_2O_5 or P_4O_{10}. The simpler formulas for the last two oxides are the ones which are the more commonly used for these substances, but the more complicated ones correspond to their molecular weights.

Phosphorus pentoxide is a white powder which is formed when phosphorus burns in dry air. It is exceedingly hygroscopic, and instantly combines with water to form metaphosphoric acid, HPO_3. It is the most thorough drying agent known much better than sulfuric acid and far better then calcium chloride. Owing to its great affinity for water, it will even withdraw the elements of water from compounds containing hydrogen and oxygen. Its use in the preparation of nitric anhydride depends upon this property.

The trioxide is formed when phosphorus burns in a limited supply of air. It differs from the pentoxide in that it has a low melting-point, 22.5°, and boiling-point, 173°, and hence may be easily separated from the higher oxide by distillation. It is orless. With cold water it reacts very slowly forming phos- orous acid, and hence is often called phosphorous anhydride.

Acids of Phosphorus.—Phosphorus pentoxide is the anhydride three important acids, metaphosphoric acid, HPO_3, pyro- osphoric acid, $H_4P_2O_7$, and orthophosphoric acid, H_3PO_4. nese are formed by the interaction of varying quantities of ater and the anhydride:

$$
\begin{aligned}
P_2O_5 + H_2O &= 2HPO_3 \\
P_2O_5 + 2H_2O &= H_4P_2O_7 \\
P_2O_5 + 3H_2O &= 2H_3PO_4
\end{aligned}
$$

n addition to these three acids there are the less important ones, hosphorous acids, H_3PO_3, hypophosphoric acid, $H_4P_2O_6$, and ypophosphorous acid, H_3PO_2. The pentoxide is not the anhy- ride of these last three acids and it will be noticed that the alence of the phosphorus is 3, 4 and 1 respectively.

Orthophosphoric acid is of greater importance than any other cid of phosphorus and is always in mind when phosphoric acid mentioned without qualification. It may be prepared as in- icated above, or obtained from its salts by the second general ethod for the preparation of acids. The first general method not available since the acid cannot be distilled. It is most nveniently made in pure state by oxidizing ordinary phos- horus with dilute nitric acid, nitric oxide being formed at the me time. By concentrating the solution, the excess of nitric id is driven off. The orthophosphoric acid obtained in this y is a thick viscous liquid which crystallizes slowly and with ficulty. The melting-point of the pure acid is 41°.

Its solution in water reddens litmus and has a pure agreeable id taste. It is not very strongly dissociated. A solution one gram equivalent of phosphoric acid in a liter of water ntains only about one-fourteenth as much hydrogen as ion as hydrochloric acid solution of the same concentration.

Orthophosphoric acid is a tribasic acid as is indicated by its rmula, H_3PO_4. It forms three series of salts according as one, o, or all three of the atomic weights of hydrogen per mole are placed by metals. We have then normal salts and two kinds acid salts. These latter are distinguished by using Greek merals to show how many atomic weights of metal are present.

Thus we have normal sodium phosphate, Na_3PO_4, which is often called trisodium phosphate; disodium phosphate, Na_2HPO_4; and monosodium phosphate, NaH_2PO_4. The names tertiary, secondary and primary are also used to designate these salts. Solutions of the mono salt are slightly acid in reaction while those of the disodium salt are faintly alkaline, and of the tri- exceedingly so. These phenomena are connected with the fact that phosphoric acid is a weak acid and also polybasic. Like all other polybasic acids, it dissociates one atomic weight of hydrogen more strongly than the rest. The dissociation $H_3PO_4 = H^+ + H_2PO_4^-$ takes place to a fair degree, while that of $H_2PO_4^- = H^+ + HPO_4^{--}$ is slight, and HPO_4^{--} scarcely breaks down at all into H^+ and PO_4^{---}. Because of the weakly acid character of the ions HPO_4^{--} and $H_2PO_4^-$, the trisodium salt is almost completely hydrolyzed into the disodium salt and sodium hydroxide, and the disodium phosphate is also slightly affected.

The phosphates which occur in nature are the normal salts and the principal one is that of calcium, $Ca_3(PO_4)_2$. This salt is almost universally present in the soil. It is, however, very slightly soluble so that it is only slowly available as a source of phosphorus compounds for plants. Monocalcium phosphate, $Ca(H_2PO_4)_2$, is easily soluble and makes an excellent fertilizer. It is known in commerce as "superphosphate" and is prepared by treating calcium phosphate with dilute sulfuric acid from the lead chambers. So extensive is the use of phosphate fertilizers that the larger part of the sulfuric acid made is used in their manufacture.

Pyrophosphoric Acid.—When orthophosphoric acid is carefully heated to about 250°, it loses water and is changed into pyrophosphoric acid, $H_4P_2O_7$,

$$2H_3PO_4 = H_4P_2O_7 + H_2O$$

When dissolved in water, it gradually reacts with the latter forming the ortho acid. The formula indicates that it is tetrabasic, and it forms four series of salts, $NaH_3P_2O_7$, $Na_2H_2P_2O_7$, $Na_3HP_2O_7$, and $Na_4P_2O_7$. Of these the second and fourth are the best known.

Metaphosphoric Acid.—Metaphosphoric acid, HPO_3, may be obtained by heating orthophosphoric acid to a higher tempera-re than that required for the preparation of pyrophosphoric id, or by adding the proper amount of water to the pentoxide.

Metaphosphoric acid melts at a rather high temperature and lidifies to a wax-like mass on cooling. It is put on the market the form of transparent sticks and is known in commerce as acial phosphoric acid. These sticks are hard and glass-like ecause they contain a little sodium metaphosphate. At high mperatures it passes into vapor, and in this state has the forula $(HPO_3)_2$ as is shown by its molecular weight.

At room temperatures, a solution of metaphosphoric acid is hanged rather rapidly into pyrophosphoric acid and the latter hen more slowly into the ortho acid.

The sodium salt of metaphosphoric acid is formed by heating nonosodium orthophosphate to a high temperature,

$$NaH_2PO_4 = NaPO_3 + H_2O$$

r by heating sodium ammonium phosphate, $NaNH_4HPO_4$,

$$NaNH_4HPO_4 = NaPO_3 + NH_3 + H_2O$$

Sodium metaphosphate fuses to a clear glass-like mass and in the fused state is able to dissolve most of the oxides of the metals, receiving from them in many cases, colors characteristic of the netals. This property is made use of in blowpipe analysis.

Phosphorous Acid.—Phosphorous acid, H_3PO_3, is formed by he action of cold water upon phosphorus trioxide, P_4O_6, or of ater upon the tri-chloride, bromide, or iodide of phosphorus. Its rmula indicates that it is a tribasic acid, but it will form only o series of salts, NaH_2PO_3 and Na_2HPO_3. This property probably due to an extreme case of the difference in the degree dissociation of the hydrogens of a polybasic acid, to which tention was called under phosphoric acid.

Phosphorous acid is a crystalline solid melting at 70°. When eated strongly, it decomposes into phosphine, metaphosphoric id, and water. It is a powerful reducing agent, being oxidized phosphoric acid.

Phosphorus Sulfides.—By heating red phosphorus and sulfur gether in the proper proportions in the absence of air, a rapid action takes place, and according to the relative proportions of e substances, the sulfides P_4S_3, P_2S_3, P_3S_6, and P_2S_5 [illegible]d.

Of these sulfides, P_4S_3 is the most important, because of its use in matches. It does not take fire spontaneously, but does so when gently heated. Red phosphorus is used because the reaction is too violent with yellow.

With water the sulfides react to form hydrogen sulfide and the acids of phosphorus.

Applications of Phosphorus.–[illegible] far the greater part of the phosphorus made is used in the [illegible]ufacture of matches. These may be divided into two cla[illegible]hose which will strike anywhere, and those which will ig[illegible]y when rubbed on a specially prepared surface. The first kn[illegible] made by dipping the sticks into melted paraffin, and then [illegible]o a paste containing glue, powdered glass, iron oxide, le[illegible]ide, and phosphorus sesquisulfide, P_4S_3. The phosphorus [illegible]e is enclosed within the mass and so protected from the air. [illegible]pon striking the match the friction raises the temperature, at the point of contact, above the kindling point of the phosphorus sulfide. The whole very combustible mixture in the head then burns and sets fire to the wood. These matches are so easily ignited that they are liable to produce accidental fires. This type of match was formerly made with free phosphorus and was highly poisonous, but the kind containing phosphorus sulfide is practically non-poisonous.

The second kind is the safety match which lights on the box. The head of this match may contain potassium chlorate and dichromate, sulfur, manganese dioxide, iron oxide, powdered glass, glue, and gum arabic, but no phosphorus. The striking surface on the box is composed of a mixture of red phosphorus, antimony trisulfide, dextrine, and lampblack. Safety matches may sometimes be ignited by friction on a non-conducting surface such as that of glass. Since these matches contain no ordinary phosphorus they are relatively non-poisonous and can be manufactured without injury to the workmen. For the reason that it is practically impossible that they should be ignited accidentally, this form of match is much superior to the other for domestic purposes. In the laboratory red phosphorus is used wherever possible, because it is more moderate in its action and less dangerous than the yellow.

CHAPTER XVI

CARBON

General.—Carbon belongs to a family of elements, which in eir highest state of oxidation are tetravalent; the other memers of the family are silicon, germanium, tin, and lead. Carbon nd silicon are non-metallic elements, while the others are metals nd will be discussed later. The compounds of carbon are xceedingly varied, more than a hundred and fifty thousand of hem being known. In fact, the chemistry of carbon is so comlex that it is considered a separate branch, and is called organic hemistry. It received this name because all living organisms ontain carbon compounds, and it was for a long time supposed hat most of these substances could be produced only by the ife processes of such organisms. At the present day so many of these compounds have been synthesized in the laboratory that we are now of the opinion that it is possible to prepare any carbon ompound artificially.

The great importance of the compounds of carbon may be ealized when we consider that nearly all of our foods, and most f our medicines, consist essentially of these substances, and hat the principal source of the energy which we use in our arious industries is the carbon in coal, gas, oil, etc.

Occurrence.—Carbon occurs free in nature in two distinct llotropic crystalline modifications, which are known as diamond nd graphite. A third form of elementary carbon, known as morphous carbon, or charcoal, may be obtained by heating rganic substances, such as wood, sugar, etc., to a high temperaure in the absence of air. Many persons consider that amorhous carbon is present in coal and so would say that this form f carbon occurs in nature. In combination, carbon is found as n essential constituent of all living organisms; as carbon dioxide the air and water; as calcium carbonate in the great beds of mestone; as very complex compounds chiefly in co with hydrogen in coal and oil; and as methane, CH_4, in natural gas.

Diamond.—As is well known, diamond is a clear colorless substance which crystallizes in octahedrons and is exceedingly hard. Because of these properties, its rarity and the fact that it has a very brilliant luster, diamond has long been valued highly as a gem. The principal loc s in which diamonds are found at the present day are Brazil a South Africa. In Brazil, they are obtained from alluvial dep s, while in South Africa they occur within and in the imm iate vicinity of old volcanic chimneys. The diamonds ha pparently been formed from carbon under great pressure, a high temperature of the lava. They are usually small, very r ly weighing more than a few grams; but one, the Cullinan mond, was found in 1905 at Premier mine in Transvaal which weighed 620 grm., or 3,024 carats, or 1.37 lb., and even then the stone was evidently merely a fragment of a much larger one.

Very small diamonds have been prepared artificially by Moissan. He placed charcoal made from sugar in cast-iron heated to a very high temperature in an electric furnace and then cooled the iron as rapidly as possible. Under these conditions a rigid shell of solid cast-iron was quickly formed around the outside of the mass, while the interior still remained molten. Now cast-iron upon solidification increases in volume, so that, as the interior gradually froze, great pressure was produced. Under these conditions the carbon was simultaneously exposed to very high temperature and pressure, and a small portion of it crystallized as minute diamonds. Because of its extreme hardness it i used for cutting and writing on glass and many other purpose where such a property is required. The density of diamond 3.5–3.6, is greater than that of the other forms of carbon. Whe diamonds are heated in the air, or oxygen, they burn to carbo dioxide. Toward most chemical reagents it is very indifferent.

Graphite.—Graphite is the second crystalline modification c carbon. It occurs in many localities, chiefly Austria and Ceylo in rather poorly formed rhombohedral crystals. It is black i color, non-transparent, so soft that it may be readily scratche with the finger nail, and leaves a black streak on paper, has density of 2.25, and so differs radically in its properties fro diamond. It is prepared artificially on a large scale by heating petroleum coke, anthracite coal, or any other nearly pure form of carbon, to a very high temperature in the electric furnace (Fig. 40). Graphite is highly resistant to chemical action, but rather less so than diamond. When heated in the air, or oxygen, it slowly burns to carbon dioxide. When heated alone it undergoes no change until the highest temperature of the electric arc is reached, when it passes slowly into vapor without melting. Because of its infusibility, graphite when mixed with a small portion of clay to act as a binder, is used in making crucibles which have to stand high temperatures. Because of these same properties and the further fact that it is a good conductor of electricity, graphite is extensively used at present for making electrodes for use in electric furnaces and in the electrolytic industries. Crystals of graphite very easily break up into fine scales which slip over one another with but little friction. On this account it is often used as a lubricant. Finely ground graphite mixed with clay and slightly baked, constitutes the "lead" of our lead pencils. The more clay the harder the pencil.

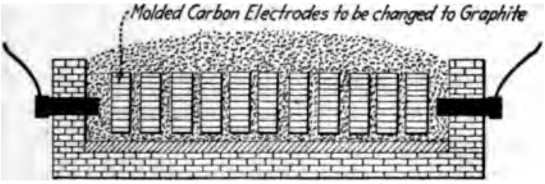


FIG. 40.

Amorphous Carbon.—As has been mentioned above, amorphous carbon is prepared by heating certain carbon compounds to a high temperature in the absence of air. A rather large number of different forms are distinguished according to their state of division and the substances from which they were formed. We have, for example, charcoal of various kinds, soot or lamp black, and coke. The density, hardness and electrical conductivity of all forms of amorphous carbon increase with the temperature to which they are heated. At the highest temperatures of the electric furnace, the various forms of amorphous carbon are transformed into graphite. Like graphite, amorphous carbon is infusible. It is, however, much more easily combustible than graphite.

Soot is a comparatively pure form of finely divided carbon and is formed by the combustion of various carbon and hydrogen compounds with an insufficient supply of air. It is very soft, intensely black, has a small density, is easily combustible, and is a good non-conductor of heat [illegible] tricity. It finds application as a pigment in printer's i [illegible] t, etc., under the name of lampblack.

Charcoal.—The most con [illegible] rm of charcoal is that prepared by heating wood to fairly [illegible] igh temperature in cast iron retorts. In addition to the char [illegible] al, methyl or wood alcohol, CH_3OH, acetic acid, CH_3COO [illegible] l creosote are formed and are condensed, separated and [illegible] more than the value of the charcoal. Bone charcoal or [illegible] lack as it is called, is made by carbonizing bones in retorts. At the same time a valuable by-product known as bone oil is produced. All solid substances seem to have a tendency to increase, right at their surface, the concentration of any gaseous substance with which they may be in contact. This property is called adsorption. It is shown strongly by all forms of charcoal, especially by those such as bone and cocoanut shell charcoal which have per unit weight very large surfaces owing to the fineness of the pores of the materials from which they were made. The higher the molecular weight and boiling point of the gas and the lower the temperature, the greater is the adsorption.

When cooled to the temperature of liquid air, cocoanut shell charcoal will adsorb very completely all gases except hydrogen, helium and neon. One of the most convenient ways for producing a high vacuum is to seal a bulb containing cocoanut charcoal to the vessel to be exhausted and then cool the bulb with liquid air. In a short time, the air in the vessel will be so completely taken up by the charcoal that a very high vacuum will be produced.

When charcoal is added to solutions it adsorbs nearly every substance present. This is more pronounced with bone-black than other charcoals for the reason given above. Here again, the adsorption is more complete the higher the molecular weight of the substance affected, and since coloring matters are usually very complex, they are adsorbed to a greater extent than most ther substances. Crude sugar contains a coloring matter which removed in refining by boiling a solution of the sugar with one-charcoal. Some of the sugar is adsorbed, but not enough o make a serious loss. Charcoal is a catalyzer for many reactions, particularly between gases. Here again we are dealing with a surface phenomenon, and the charcoals prepared from the more finely cellular substances are the more active.

Coal may be considered natural charcoal, and has probably een formed by the partial decomposition of vegetable matter nder water. Various varieties of coal are distinguished, such s anthracite, semi-anthracite, bituminous, and lignite. These iffer rather widely in the relative proportions of carbon, hydroen, nitrogen, oxygen, sulfur, and mineral matters which they ontain, the anthracite being the nearest pure carbon, and the thers decreasing in purity in the order named. The world's production of coal is about 1,300 million tons and that of the United States about 500 million tons each year.

Coke is formed by heating bituminous coal with the exclusion of air until practically all the volatile matter has been distilled off. The gases given off are rich in compounds of carbon and hydrogen, and are very valuable for fuel and illuminating purposes. In addition, they contain many useful products, such as ammonia, benzene, C_6H_6, coal tar, etc. Coke is largely used as a fuel in blast furnaces and many other metallurgical operations, since it produces a very high temperature, burns without smoke and contains a relatively small amount of sulfur.

Relation Between the Allotropic Modifications.—Although the various modifications of carbon differ so radically in their properties they are really composed of the one element carbon, and contain nothing else, as is shown by the following argument. When equal weights of pure diamond, graphite, or amorphous carbon are burned in oxygen, equal weights of carbon dioxide are produced in each case, and nothing besides carbon dioxide is formed in any case. The heat of combustion of the various modifications is different so that in this, as in other cases, the allotropic modifications differ in their energy content. Because of the non-volatility and insolubility of carbon, it is impossible to determine its molecular weight. Its atomic weight, however, is 12.005.

Oxygen Compounds.—Carbon forms two well known oxides, the monoxide CO, and the dioxide CO_2. The second of these compounds is by far the more important.

Carbon Dioxide.—Carbon dioxide, CO_2, is a gaseous substance whose molecular weight is 44. It is colorless, has a very feeble taste and odor, its critical temperature is 31°, and its critical pressure is 73 atmospheres.

Liquid carbon dioxide is a common article of commerce. It is sold in very strong cylinders. At a temperature of 20° its vapor pressure is 58.5 atm. or 860 lb. to the square inch, so it may be easily seen that the cylinder should be well constructed and handled with care. The principal use for this carbon dioxide is in the manufacture of soda water and other carbonated beverages. The boiling-point, or rather subliming-point of carbon dioxide is $-78.2°$; the freezing-point is considerably higher than this $-57°$; so that at ordinary pressures liquid carbon dioxide cannot exist in open vessels. Liquid carbon dioxide is a colorless, very mobile substance, which is but slightly soluble in water. It is not a conductor of electricity, does not act as a solvent toward most substances, and does not redden litmus paper; in short, it does not present any striking chemical properties.

Solid carbon dioxide may be formed by allowing the liquid modification to flow out from the cylinder at any temperature below the critical temperature of the liquid. As soon as the liquid comes in contact with the air, the greater portion of it is at once turned into vapor. The heat necessary for this transformation is absorbed largely from the carbon dioxide itself, and so far cools a portion of this that it assumes the solid state, although its temperature in this condition is $-78.2°$.

The solid carbon dioxide is a white snow-like substance which is very convenient for use as a cooling agent, since we can so easily get with it the definite temperature of $-78.2°$. In order to secure better thermal contact with the substance to be cooled, it is commonly mixed with ether. By diminishing the pressure upon the carbon dioxide, temperatures lower than $-78.2°$ may be obtained. In this way by causing it to evaporate in a vacuum, a temperature of $-100°$ may be reached.

Carbon dioxide occurs in nature in very large quantities. The air contains three to four parts of this substance to ten thousand rts by volume. It escapes in great volumes from volcanoes, ineral wells and springs, and at various places on the earth it sues in an almost pure state from fissures. It is formed during he breathing of animals and in the fermentation and decay of rganic substances. It may be prepared by burning carbon or ny carbonaceous material in an excess of oxygen or of air; or y heating limestone, calcium carbonate, $CaCO_3$, in lime kilns here it breaks down into calcium oxide, CaO, and carbon dioxide, CO_2;

$$CaCO_3 \rightleftarrows CaO + CO_2$$

r by the action of an acid upon a carbonate. The carbon dioxide which is put on the market in the liquid form is very rgely obtained from lime kilns and from the fermentation ats of the breweries. The ordinary laboratory method for its reparation is to place some pieces of marble, which is a very ure form of calcium carbonate, in a flask and allow hydrochloric acid to run slowly upon them. Under these conditions the carbon dioxide is given off in a steady stream,

$$CaCO_3 + 2HCl = CaCl_2 + CO_2 + H_2O$$

Being heavier than air and not very soluble in water, it may be collected either by the displacement of air or over water. Carbon dioxide is neither a supporter of combustion nor of animal life. Air containing 4 per cent. of carbon dioxide will extinguish a candle flame, but will support respiration for a short time. Since carbon dioxide is heavier than air and is being gradually given off by the earth, it often accumulates in old wells, cellars, cisterns, etc., in quantities sufficient to render it dangerous to persons entering such places. The presence of carbon dioxide in dangerous quantities may be easily detected by the lowering of a lighted antern. If the flame is extinguished no one should enter until he excavation has been thoroughly ventilated.

It dissolves in its own volume of water at ordinary temperatures and the solubility follows Henry's law.

The solution has a feebly acid reaction and contains the very nstable substance, carbonic acid, H_2CO_3. This is a very weak ibasic acid which forms two series of salts, the normal and he acid carbonates. Because of the weakness of carbonic acid, he easily soluble normal salts are rather strongly hydrolyzed and are alkaline in reaction; and the so-called acid salts are almost neutral in their reaction. The most abundant naturally occurring carbonate is that of calcium, $CaCO_3$. Sodium carbonate, Na_2CO_3, is manufactured in enormous quantities from sodium chloride, and is a very important chemical. Sodium, potassium and ammonium carbonates are soluble in water. Most of the other carbonates are not soluble.

When an acid is poured on rbonate, the carbonic acid formed decomposes at once wit risk effervescence due to the escape of carbon dioxide. Such a ervescence suggests a carbonate but does not prove its pre because a few other salts, sulfites and sulfides, for exampl ll also effervesce. The best test for carbon dioxide is the fo tion of a white precipitate of calcium carbonate when it i ought in contact with lime water, which is a solution of cal hydroxide in water. The carbon dioxide is first dissolved by the water forming carbonic acid, which then reacts with the calcium hydroxide for the formation of water and the difficultly soluble calcium carbonate,

$$CO_2 + H_2O \rightleftarrows H_2CO_3$$
$$Ca(OH)_2 + H_2CO_3 = CaCO_3 + H_2O$$

Because of the fact that carbon dioxide will combine with water for the formation of carbonic acid, it is often called carbonic anhydride.

Circulation of Carbon.—During the breathing of animals oxygen is taken up from the air in the lungs forming an unstable compound with the hemoglobin of the blood. It is then carried to all parts of the body and gradually oxidizes the complex compounds contained therein, forming carbon dioxide as one of the products; this is carried by the blood to the lungs and there given up to the air and expired. In the dark practically this same process takes place in plants, but in the light those plants which contain green coloring matter in their leaves are able to bring about the reverse change, partially breaking up the carbon dioxide absorbed from the air, liberating a part of its oxygen in the free state and combining the residue with water for the formation of complex compounds of which the sugars, starches, and celluloses are prominent examples. These compounds are food for plants as well as for all animals, hich live directly or indirectly upon them. This decomposition carbon dioxide and the building up of complex compounds from takes place only under the simultaneous influence of chlorоyl, the green coloring matter of plants, and of light. It is companied by the absorption of a great amount of energy ich is obtained from the light of the sun. The energy so sorbed is given out once more when these complex compounds rn, decay, or oxidize in the bodies of animals; and so the ultiate source of the energy of animals and of all engines, which e driven by the burning of wood and other vegetable products, the light of the sun. Coal has been formed by the partial composition of vegetable organisms, and the energy obtained om it was originally absorbed by these organisms from the ht of the sun; so the steam engine of to-day is really driven by e energy of the sunlight of thousands of years ago.

By this cycle of changes, carbon dioxide is successively taken from and given back to the air, and thus there is in nature a rt of circulation of carbon. The energy, however, accompanyg these transformations apparently does not move in any such cle; that given out during the decomposition of the complex mpounds is not available for the re-formation of these subances, and this change can take place only with the influx of fresh supply of energy from the sun. We are to think of the ergy relationships in the following way: A stream of energy mes to the earth in the sunlight; a very small part of this is bsorbed by the green plants and stored as chemical energy in e form of complex carbon compounds, which are available for se as foods, or combustibles, and so furnish us with the greater art of the energy which we employ The other sources of ergy which man employs, water power and the wind, are ally dependent upon the sun, so that we owe practically all our stores of available energy to this body.

Photochemical Action.—Red and yellow light rays are pracally the only ones which have any influence on the reactions hich take place in plants; while in the photochemical changes in otographic plate, the red rays are almost inactive and blue, een and violet produce most of the effect. From these and milar instances, it *follows* that every kind of light can produce me kind of *chemical change*.

Carbon Monoxide.—Carbon monoxide is a gaseous substance which is formed when coal is burned in a limited supply of air It may also be prepared by the action of carbon at a high temperature upon carbon dioxide. The carbon monoxide burns in the air with a pale blue flame, and it is the burning of this substance which produces the blue flames that are so commonly seen at the top of a hard coal fire. The chemical changes taking place in such a fire are mainly as follows: When the air first comes in contact with a hot carbon at the bottom of a firebox, carbon dioxide is formed, which, passing up through the body of the coal, is reduced to carbon monoxide; this burns when it comes in contact with the air at the surface of the fire. The equations for the reactions are as follows,

$$C + O_2 = CO_2 \text{ and } CO_2 + C \rightleftarrows 2CO$$

These reactions take place on a large scale in the manufacture of "producer gas" for fuel and power purposes, see p. 250, and also in the iron blast furnace.

When steam is passed over highly heated carbon, carbon monoxide and hydrogen are produced as shown in the equation

$$C + H_2O = CO + H_2$$

This is one of the reactions which takes place in the technically important process for making what is known as water gas. This will be discussed in some detail later, see p. 250.

Carbon is an excellent reducing agent and is much employed for this purpose in the extraction of metals from their oxides. When this change takes place at a high temperature, as is usually the case, carbon monoxide is formed. The equation for the reduction of zinc oxide is

$$ZnO + C = Zn + CO$$

Carbon monoxide is often prepared by heating oxalic acid, a white crystalline substance, whose formula is $H_2C_2O_4$, with sulfuric acid. Under these conditions the oxalic acid decomposes into carbon dioxide, carbon monoxide and water,

$$H_2C_2O_4 = CO_2 + CO + H_2O$$

The carbon dioxide is removed by passing the mixture of gases through a strong solution of sodium hydroxide. Formic acid

ted with sulfuric acid breaks down into water and carbon
noxide,

$$HCOOH = CO + H_2O$$

this reaction and that of oxalic acid the sulfuric acid appar-
tly does nothing except take up the water formed.

Properties.—Carbon monoxide is a colorless, tasteless gas with
very faint, peculiar odor, very slightly soluble in water. Its
lecular weight 28, critical temperature −140° boiling point −
0° are nearly the same as those for nitrogen. Carbon monoxide
ll combine directly with oxygen, chlorine, and many other sub-
nces. With oxygen, carbon dioxide is formed with the
olution of much heat, making it an excellent fuel. It combines
th chlorine forming the substance, $COCl_2$, carbonyl chloride
phosgene. This combination takes place when carbon monox-
e and chlorine are exposed to sunlight, or when a mixture of
e two gases is passed over animal charcoal which acts as a
talyzer.

Carbon monoxide is a powerful reducing agent. The reduc-
on of iron oxide to metallic iron by this gas takes place on an
ormous scale in the blast furnace. The reaction may be
presented by the following equation:

$$Fe_2O_3 + 3CO = 2Fe + 3CO_2$$

Carbon monoxide is extremely poisonous. This is connected
ith the fact that it will combine with the hemoglobin of the
lood to form a very stable compound which is unable to take
p the oxygen of the air. So poisonous is carbon monoxide that
0 c.c. of the gaseous substance will be sufficient to kill an
verage man.

Carbon Disulfide.—When charcoal is heated to a rather high
mperature in the vapor of sulfur, the elements combine forming
n easily volatile liquid substance, called carbon disulfide, CS_2.
his substance is now manufactured on a large scale in electric
rnaces (Fig. 41). It is a colorless liquid whose boiling-point
46°. It has a very high index of refraction for light. When
erfectly pure it has a pleasant ethereal odor; the commercial
rticle, however, contains impurities which gives it a very
isagreeable smell. It is an excellent solvent for sulfur, iodine,
hosphorus, rubber, resins, and fats and hence finds extensive use

in the arts and manufactures. A mixture of carbon disulfide vapor and air is violently explosive and is remarkable for the fact that ignition takes place at temperatures as low as 260°. On this account even greater care must be taken in handling this substance than is used with gasoline.

Nitrogen Compounds of Carbon.—At the very high temperature of the electric arc, car [illegible] itrogen will combine directly w [illegible] ormation of a gaseous compou [illegible] **anogen,** C_2N_2. This substan [illegible] also be obtained by heating mercu [illegible] cyanide, $Hg(NC)_2$. This breaks [illegible] wn into metallic mercury and cyanog [illegible] as shown in the equation,

$$[illegible](NC)_2 = Hg + C_2N_2$$

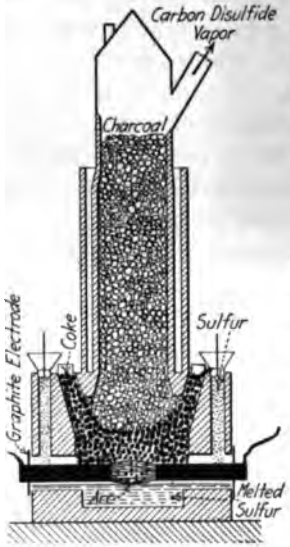


Fig. 41.

Cyanogen is a colorless gas, having a peculiar pungent odor resembling that of peach kernels; it is exceedingly poisonous and burns in the air with a characteristic red-violet flame, forming carbon dioxide and nitrogen. Its stability at high temperature is due to its being formed from the elements with the absorption of heat.

Chemically, cyanogen resembles the halogens. It forms a series of salts called cyanides, which are similar to the chlorides, but contain the group NC, instead of chlorine. Silver cyanide, for example, is a difficultly soluble white substance, which is very much like silver chloride in its general properties. From these salts, **hydrocyanic acid** or prussic acid, HNC, may be easily obtained by the addition of a less volatile acid and distilling. It is a colorless liquid which boils at 27° and has a very strong odor like that of peach pits. It is one of the weakest acids. On this account, the soluble cyanides react strongly alkaline when in solution in water, owing to hydrolysis. Hydrocyanic acid and the cyanides are extremely poisonous substances. The poisonous effect of the peach pits is due to hydrocyanic acid formed by the action of water upon a substance called ygdalin which is in the pit. Not only is hydrocyanic acid oison toward animals, but it will also stop or "poison" the ion of many catalyzers, and it is thought that perhaps the sonous action of this substance on animals is due to its stopg the catalytic processes which are going on within them.

yanates.—Cyanides are good reducing agents, and when dized often form compounds called cyanates, potassium inate, KNCO, for example, is formed by cautiously oxidizing assium cyanide, KNC. Cyanic acid, corresponding to these inates is very unstable. It is a colorless liquid with a strong ell resembling that of acetic acid.

Thyiocyanates.—When a cyanide is heated with sulfur, the two bstances combine to form a thiocyanate. These correspond the cyanates. The formation of potassium thiocyanate, NCS, is shown in the following equation,

$$KNC + S = K\,NCS$$

ne thiocyanates are used as reagents for detecting the ferric lts with which they give an intense red coloration.

The Hydrocarbons.—Several hundred compounds of carbon nd hydrogen have been described. For purposes of classificaon and as an aid in getting a comprehensive view of their relaons, they have been divided into several series according to the omposition and general properties of the substances. The rincipal series is that known as the Marsh Gas or Paraffin series, nd the simplest member of this is marsh gas or methane. This eries is distinguished by the fact that in all the compounds elonging to it carbon has a valence of 4—the highest valence which it is capable of taking on. For this reason, the members f this series are sometimes called the saturated hydrocarbons. igure 42 gives the names and formulas, and indicates the meltng- and boiling-points of some of the more important of the lower nembers of the normal paraffins.

An inspection of this figure will show that the boiling- and nelting-points of these hydrocarbons increase as they become nore complex. It will be noticed, too, that the formula for each ucceeding member of the series differs from that of the one which ust precedes it by CH_2. A series of carbon compounds which re related to one another in this way is called a **homologous**

series. The members of such a series have similar properties which gradually change with the composition of the compound. The change in the boiling-points of the compounds shown in the figure is an illustration of this. Most of these hydrocarbons occur in nature in large quantities, the majority of them being found in crude petroleum, while methane and ethane are present in natural gas.

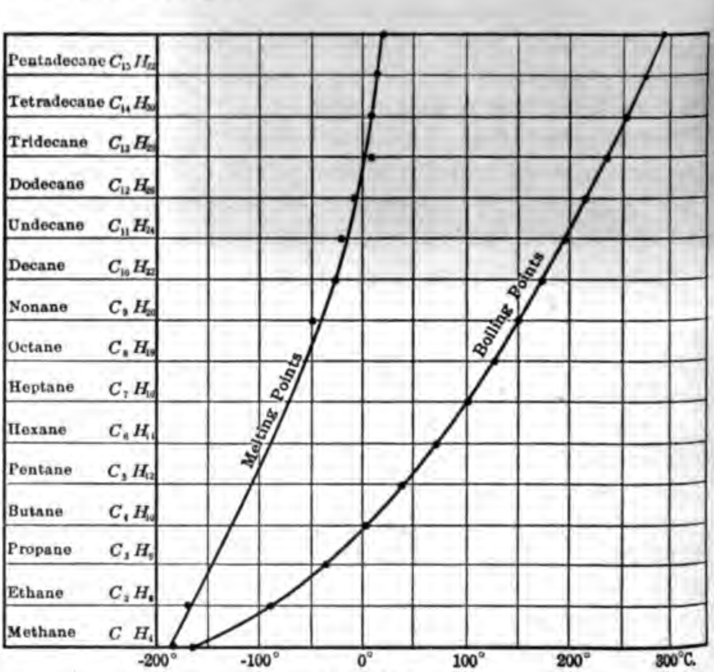


FIG. 42.

Crude Petroleum.—Crude petroleum or "oil" is found in many places in the United States, in Ontario, in Baku on the Caspian Sea, in Roumania, in India, and in Japan. This oil is a mixture of a great many substances, but principally of hydrocarbons, and usually consists very largely of the hydrocarbons of the marsh gas series. In oil refining, for commercial purposes, no attempt is made to prepare pure substances from the oil, but the more volatile portions are distilled off and separated into fractions according to their density and adaptability for particular

ses. The following table gives the name, approximate
onents, density, and uses for some of the more common
cts.

Some Commercial Petroleum Products

e name	Chief constituent	Density	Use
line.....	Pentane..............	0.6222	Solvent; automobiles.
ie......	Hexane..............	0.6511	Solvent; automobiles.
ne......	Heptane..............	0.722–0.737	Solvent; automobiles.
ha.....	Octane...............	0.745–0.824	Traction and stationary engines.
ene.....	Nonane, decane, etc...	0.791–0.824	Illuminating; fuel; and stationary engines.

e residue left after removing these substances is then
led in a current of steam. Some of the higher boiling
ıcts which come over under these conditions are used
ıbricating oils, but must first be purified from the solid
bers of the series by cooling to a low temperature and
ing with the aid of filter presses. The solid substances so
ed constitute what is known as **paraffin**, while the low
ng product, which is salve-like at ordinary temperatures, is
l **vaseline**. The final residue left in the retort is used as
ılt. Natural asphalt is a mixture of hydrocarbons which
s in nature. Just how these hydrocarbons are formed
ture is not known, but they have probably been produced,
ıst cases at any rate, by the partial decomposition of animal
egetable organisms, although it is possible that they may
resulted from the action of water upon carbides, compounds
bon with metals.

ıst of the hydrocarbons are rather indifferent chemically.
are not acid like hydrogen chloride nor basic like ammonia.
of course burn in oxygen, forming carbon dioxide and water,
eact with chlorine or bromine to form compounds. When
d to a very high temperature they all show a tendency to
down into hydrogen, carbon and simpler hydrocarbons
ining a relatively smaller amount of carbon. The process

is technically known as "cracking" and is now used on a large scale to increase the yield of gasoline.

Methane.—Methane or marsh gas, CH_4, is the first member of the paraffin series. It is the principal constituent of natural gas. It is formed during the decay of vegetable matter in the bottom of ponds and marshes, and to this fact it owes its name, marsh gas. It is found in [illegible] able quantities in coal, and since its mixture with air is [illegible] ive, it is one of the causes of the disastrous coal mine [illegible] ons. When found in mines it is often called "fire-da [illegible] e miners, while the carbon dioxide, which is formed wh [illegible] urns and is left in the mine after an explosion, is called [illegible] -damp." The critical temperature of methane is -82° [illegible] critical pressure 56 atmospheres; its boiling-point is [illegible] Because of its very low critical temperature, the meth [illegible] f natural gas does not exist in the depths of the earth in a liquid condition, but is present simply as a highly compressed gas, filling the pores of the rocks.

The origin of methane found in nature is as much in doubt as that of the other hydrocarbons, but the probabilites are that it was formed by the decomposition of organic matter. It may be made by the action of water upon aluminum carbide,

$$Al_4C_3 + 12H_2O = 4Al(OH)_3 + 3CH_4$$

and it is possible that a part of the methane has been produced by this reaction. In the laboratory the gas is usually prepared by distilling a dry mixture of sodium acetate and sodium hydroxide. The equation for the reaction is as follows,

$$NaC_2H_3O_2 + NaOH = Na_2CO_3 + CH_4$$

Methane burns in the air forming carbon dioxide and water. The flame has very little luminosity, unless used with a Welsbach mantle composed of the oxides of cerium and thorium. Because of the great amount of heat which is produced during the combustion, methane is very valuable for fuel and in the form of natural gas is much used for this purpose. As will be seen by the following equation, $CH_4 + 2O_2 = CO_2 + 2H_2O$ one volume of methane will require two volumes of oxygen or ten volumes of air for complete combustion. The explosive qualities of a mixture of gas and air are utilized as a source of energy in the gas engine.

When a mixture of chlorine and methane is exposed to sunlight the four combining weights of hydrogen are successively replaced by the chlorine forming the following series of compounds:

Methyl chloride	CH_3Cl
Methylene chloride	CH_2Cl_2
Chloroform	$CHCl_3$
Carbontetrachloride	CCl_4

The other product of each of these reactions is hydrogen chloride. These are not ionized when dissolved in water and hence are not salts. Chloroform is perhaps the most important of these substances and is generally prepared by the action of bleaching powder upon ordinary alcohol. It is a colorless, easily volatile liquid which is used as a solvent and as an anesthetic. Carbon tetrachloride is now being manufactured on a large scale, but not directly from methane. It is a valuable solvent and finds many applications as such, being used as a substitute for gasoline in dry cleaning, because it has the great advantage that it is not inflammable. In fact it is now being used as a fire extinguisher and is about the only thing beside carbon dioxide which will put out a gasoline fire.

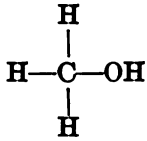
Radicals.—A study of the derivatives of methane reveals the existence of a series of compounds which have the common characteristic that their formulas can be so written that each contains a CH_3 group, CH_3Cl, CH_3Br, CH_3I, CH_3OH, $(CH_3)_2O$. When these compounds undergo certain transformations the CH_3 group seems to pass unaltered from compound to compound and so acts like a chemical individual, being like the ammonium ion in this respect. A group which behaves in this way is called a radical, and this particular group, CH_3, is known as the methyl radical. A study of the chemistry of the carbon compounds shows that we have to do with a large number of such radicals. For example, each member of the paraffin series will form a monovalent radical, which contains one less atomic weight of hydrogen per mole than the hydrocarbon from which it was formed. Ethane, C_2H_6, forms the ethyl radical, C_2H_5, propane, C_3H_8, yields the propyl radical, C_3H_7, etc. These radicals, which we have been considering are not ions, and have the remarkable property of being able to combine with almost any element or radical irrespective of the electrical character of the substance. For example, the ethyl radical will combine with sodium to form sodium ethyl, C_2H_5Na, or with chlorine forming ethyl chloride, C [illegible] yet sodium may be considered a typical electropositive [illegible], while chlorine seems to be decidedly electornegative, [illegible] ast in the chlorides. This tendency toward universal [illegible] bination exhibited by these radicals is apparently [illegible] causes for the great variety of carbon compounds. [illegible] hyl radical, for example, will combine with chlorine, [illegible], or iodine, forming methyl chloride, bromide, or [illegible] ith the hydroxyl, producing methyl alcohol, CH_3OH [illegible] oxygen yielding methyl ether $(CH_3)_2O$. If no other substance is present for it to combine with, one methyl radical will combine with another to form the compound $CH_3 - CH_3$ or C_2H_6, which is ethane, and this in turn will yield the ethyl radical, C_2H_5, which under the proper conditions will combine with a methyl radical to form the compound, $C_2H_5CH_3$, or C_3H_8, which is propane, the third member of the group. Proceeding in this way, practically the whole series of paraffin hydrocarbons has been built up and consequently they all may be regarded as derivatives of methane.

Other Hydrocarbons.—Among the hundreds of hydrocarbons, mention may be made of benzene, C_6H_6, and toluene, $C_6H_5CH_3$. These are obtained by the distillation of coal and are of great importance because they are the starting-points for the preparation of a great many very useful substances. From benzene we may make carbolic acid, C_6H_5OH, aniline, $C_6H_5NH_2$, and the aniline dyes. Toluene yields among other compounds, trinitrotoluene, $C_6H_2(NO_2)_3,CH_3$, which is a powerful explosive.

Types of Carbon Compounds.—The principal carbon compounds with which we shall have to deal may be divided into a few well-marked types; the hydrocarbons, which we have already discussed, alcohols, ethers, aldehydes, acids, esters and carbohydrates. The following table gives the general formulas for these compounds. In this table "R" stands for any monovalent radical, and "A" for the anion of a monobasic acid.

Type	General formulas
rbons	RH
	ROH
	R_2O
es	RCOH
	RCOOH
	RA
'drates	$C_mH_{2n}O_n$

Alcohols.—The first member of the alcohol group, **methyl** ›d **alcohol,** CH_3OH, is one of the by-products obtained in structive distillation of wood for charcoal. It is a color-uid, which boils at 66°. It is valuable as a fuel and as a ;. It is decidedly poisonous and is largely used in the state to mix with ethyl alcohol for the production of the ›d denatured alcohol.

molecular weight and analysis of methyl alcohol show that ,ains per molecule one atom each of carbon and oxygen ›ur of hydrogen. Experience teaches that one of the ;ens is different from the others, because sodium will : only one, forming the methylate, CH_3ONa, and further ,drochloric acid will react with the alcohol, yielding water .ethyl chloride, CH_3Cl. To represent the action with ı, one of the hydrogens must be written differently from ıers, say HCH_3O; but the action with the acid suggests a ide, and the formula, CH_3OH or  $\overset{\displaystyle H}{\underset{\displaystyle H}{H—\overset{|}{\underset{|}{C}}—OH}}$, indicates ctions, and the latter is called the structural formula for . alcohol. In a similar way, the properties of other com-ı are studied, and structural formulas devised to represent

1 alcohol, C_2H_5OH, or grain alcohol as it is called, is . by the action of an enzyme or catalyzer produced by ıpon sugars, $C_6H_{12}O_6$. The process is called fermentation ɜ equation for the reaction is as follows:

$$C_6H_{12}O_6 = 2C_2H_5OH + 2CO_2$$

The alcohol so formed may be largely separated from the water by distillation, the alcohol passing over first since its boiling-point is 78.3°. The alcohol of commerce contains about 95 per cent. by volume of alcohol and 5 per cent. of water. It is not possible to separate these two substances completely by distillation, since they form a minimum boiling mixture, boiling at 78.15° and containing 4.43 per cent. [illegible]ter. (See hydrogen chloride and water.) Absolute alcoho[illegible] from water may be obtained by adding unslaked lime to [illegible]5 per cent. alcohol. The lime combines with the water to f[illegible]lcium hydroxide, and after the action is complete, the a[illegible]hol may be distilled off. The density of alcohol at 25° [illegible] Alcohol is a valuable fuel and an extremely useful solv[illegible]ny substances which are difficultly soluble in water. [illegible]ely employed for the preparation of medicines. **Den[illegible]cohol** is 95 per cent. alcohol, mixed with some substance which cannot be readily separated from the alcohol and which will render it totally unfit for use as a beverage. A very commonly used formula is 89.5 per cent. grain alcohol, 10 per cent. wood alcohol and 0.5 per cent. benzine. Such alcohol is exempt from the payment of any internal revenue tax, and is consequently much cheaper than the pure article, and so finds extensive application in the arts.

The Ethers.—The general formula for these substances is R_2O. **Ethyl ether,** $(C_2H_5)_2O$, is the best known and by far the most important member of this group. It is prepared by heating a mixture of ethyl alcohol and sulfuric acid to 140°. The equation is

$$2C_2H_5OH = (C_2H_5)_2O + H_2O$$

The sulfuric acid acts as a catalyzer and will change many times its own weight of alcohol into ether. Ethyl ether is a colorless liquid boiling at 34.6°. It is used as solvent for fats, etc., and as an anesthetic.

The Aldehydes.—The general formula for the aldehydes is RCOH. These substances, in general, may be formed by the partial oxidation of the alcohols. The first member of the series is formaldehyde, HCOH. In this case hydrogen takes the place of the "R" in the general formula. Formaldehyde is produced by the incomplete combustion of methyl alcohol when the vapor is substance mixed with air come in contact with platinum e or platinized asbestos. Formaldehyde is gaseous at ordi- temperatures, the boiling-point being −21°; it has a very gent, irritating odor, is quite soluble in water and is put ı the market in a 40 per cent. solution, known as formalin. ı the solution and the gaseous substance are powerful germi- s and are used as disinfectants.

he Acids.—The general formula for the organic acids is OOH. These substances are numerous and important. first member of the series is formic acid, HCOOH. As the case with formaldehyde, in the formic acid the hydro- takes the place of "R" in the general formula. Sodium mate, HCOONa, is made by passing carbon monoxide over ted sodium hydroxide, the equation being

$$CO + NaOH = HCOONa$$

om this salt, the acid may be obtained by distilling it with ute sulfuric acid; concentrated sulfuric acid decomposes mic acid into water and carbon monoxide. It is a colorless uid boiling at 100°, freezing at 8.6°. Like almost all other rbon acids it is a weak acid, although somewhat stronger an acetic acid which is the next member of the series. In ite of the fact that, as its formula indicates, it contains two omic weights of hydrogen per mole, it is a monobasic acid, ly one of the hydrogens being ionizable. This fact that the drogens differ in their properties is expressed by writing them different positions in the formula—HCOOH instead of $COOH_2$. indicated by the general formula for the series, the organic ids contain the group COOH, and to this is ascribed their acid aracter, and the hydrogen of this group is supposed to be that ich ionizes.

Acetic Acid.—Acetic acid, CH_3COOH, is the second member. is formed during the destructive distillation of wood, and is of the valuable by-products of this process. Large quan- ies of the substance are produced by the oxidation of ethyl alco- by the oxygen of the air with the aid of a certain form of cteria, known as B. Aceti. The common name for this is ther of vinegar. The dilute solution of acetic acid, formed the oxidation of the alcohol contained in cider, is known as vinegar. Vinegar usually contains 4 to 5 per cent. acetic acid. Pure acetic acid is a colorless liquid which boils at 119° and freezes at 16.7°. It mixes with water in all proportions. As has been mentioned repeatedly acetic acid is a weak acid, being only slightly dissociated. Although it contains four atomic weights of hydrogen per mole, it is a monbasic acid, three of the four atomic weights of hydrogen being present in the methyl radical, and these are non-ionizable.

The Esters.—When an alcohol is acted upon by an acid, a reaction takes place which consists in the formation of water, apparently from a combination of the acidic hydrogen of the acid with the hydroxyl of the alcohol, and of an ester—a compound produced by the union of the radicals from the acid and the alcohol. The equation for the reaction between ethyl alcohol and acetic acid is as follows:

$$CH_3COOH + C_2H_5OH \rightleftarrows H_2O + CH_3COOC_2H_5$$

$CH_3COOC_2H_5$ is called ethyl acetate, and is an important member of the group of esters. Many of these are pleasant smelling substances and are largely responsible for the odors and flavors of our flowers and fruits. In addition the fats and vegetable oils are esters of the alcohol glycerine, so one of our most important classes of foods is composed of esters.

Carbohydrates.—The carbohydrates are an extensive group of carbon, hydrogen and oxygen compounds in which, with very few exceptions, the hydrogen and oxygen are present in the same relative proportions as in water, so that the general formula for nearly all members of the group may be written $C_mH_{2n}O_n$. The great importance of this class of compounds will be recognized at once when it is known that it includes sucrose (cane or beet sugar) $C_{12}H_{22}O_{11}$, glucose, $C_6H_{12}O_6$, starch, $(C_6H_{10}O_5)_x$, and cellulose, $(C_6H_{10}O_5)_y$. Cotton and linen are practically pure cellulose, and the woody part of all plants consists largely of this substance. In wood it is associated with another compoun called lignin of unknown composition. If the wood is treat with a solution of sodium or calcium acid sulfites the lignin i dissolved and the cellulose is left behind in fine fibers suitable fo making wood pulp paper. Starch is obtained from many plants iefly corn, wheat, potatoes and rice. Its importance as a food d for laundry work is well known.

When boiled with a dilute acid starch takes up water and anges to glucose; a thick syrup of the latter made from corn arch is often called corn syrup. Cane and beet sugar are idenal; their source and general properties are too well known to quire discussion beyond the fact that when boiled with dilute id, water is taken up and a solution of glucose and fructose is rmed. This process is called inversion of sugar and the product known as invert sugar.

Some Explosives.—The importance of explosives for industrial ad war-like purposes is universally recognized. Besides the oldshioned gunpowder (p. 300), and nitroglycerine (p. 207), there ay be mentioned the following: **Guncotton,** $[C_{12}H_{14}O_4(NO_3)_6]_x$, made by acting on cotton with a mixture of nitric and sulfuric cids. It is very explosive and is used in making smokeless owders; one form of these is known as walsrode. It is made of mixture of 99 per cent. guncotton, and 1 per cent. ethyl acetate. **icric acid,** $C_6H_2(NO_2)_3OH$, is made by acting on phenol, *i.e.*, arbolic acid, (C_6H_5OH), with nitric and sulfuric acids. It is the xplosive known as lyddite. **Trinitrotoluene,** $C_6H_2(NO_2)_3CH_3$, s made in the same way using toluene, $C_6H_5CH_3$, in place of phenol. It is known as T.N.T. It may be melted and poured into shells. When it explodes, great volumes of black smoke re produced. **Dynamite** is nitroglycerine absorbed in some porus material such as finely divided silica, kieselguhr as it is called. Nitric acid is used in the preparation of each of these explosives, nd this is one reason for its great industrial importance.

Unsaturated Hydrocarbons.—The methyl radical may be imagined as being formed from methane by the dropping of one tomic weight of hydrogen from this substance. If two were emoved the divalent radical CH_2 would be produced. This adical is known as methylene and forms a long series of comounds similar to those of methyl, but differing of course because f the fact that the radical is divalent. The chloride, for exmple, is CH_2Cl_2. Under proper conditions two of these methlene radicals will combine for the formation of the substance $_2H_4$, which is known as ethylene. This is the first member of long series of hydrocarbons, known as the ethylene series.

These compounds have the property of combining directly with two atomic weights of hydrogen forming members of the paraffin series. Because of the fact that they are capable of taking up more hydrogen they are called "unsaturated" hydrocarbons. They are also able to combine directly with two atomic weights of a halogen per mole of hydrocarbon. Ethylene, the first member of the series, is formed by heating ethyl alcohol with sulfuric acid to a temperature of 175°. The apparent reaction is

$$C_2H_5OH = C_2H_4 + H_2O$$

but it probably goes in steps, intermediate compounds involving the sulfuric acid being formed. It is a colorless gaseous substance and boils at −102°. Ethylene is a valuable constituent of ordinary coal gas, since it burns with a strongly luminous flame, and contributes largely to the luminosity of the gas when burned with the ordinary lava tip.

Acetylene.—If we imagine three combining weights of hydrogen removed from methane, the trivalent radical CH would b produced. Two such radicals by their combination would form the substance C_2H_2, or acetylene. This compound is still mor highly "unsaturated" than ethylene. It is the first member o another series of unsaturated hydrocarbons, known as the acetylen series. Acetylene is a colorless gas, which burns with an intensel luminous flame. When burned with oxygen in a properly constructed burner it will produce a very high temperature. Us is made of this in the metal-working trades for the autogenou welding of metals and also for the rapid cutting of steel, etc., b burning a path through it.

Acetylene is prepared by the action of water upon calciu carbide, CaC_2, the equation being as follows:

$$CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2$$

When mixed with air, in any proportions between 2.53 per ce and 73 per cent. acetylene will explode. These limits are wid than for any other gas. A mixture of natural gas and air, f example, explodes only when it contains from 5 to 15 per cent. methane, CH_4. Liquid or highly compressed acetylene is explosi even when unmixed with air, because it is formed from its e ments with the absorption of much heat; so if decompositi tarts, the heat evolved will raise the temperature and make action go faster. This is the case with all explosives. tylene is very soluble in an organic substance called ace- $(CH_3)_2CO$, which belongs roup of compounds called tones, which we have not sed. This solution in ie is not explosive and ers containing it under re are used to supply ene for the lights on iobiles and for the illumi- of isolated residences.

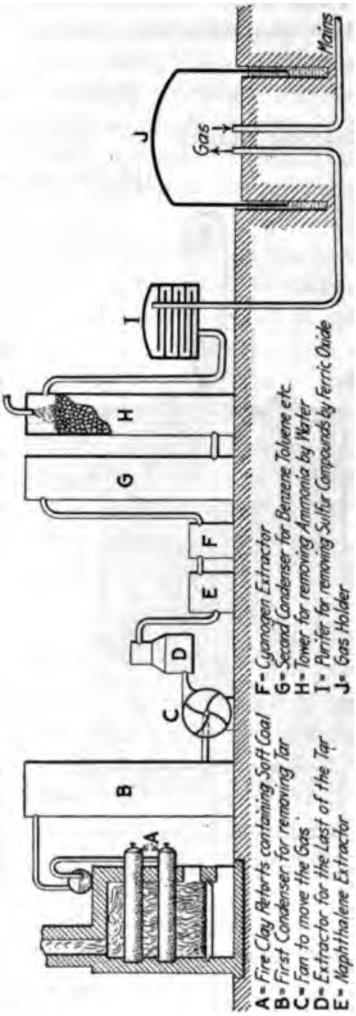

Mains
Gas
J
I
H
G
F
E
D
C
B
A
A-Fire Clay Retorts containing Soft Coal
B-First Condenser for removing Tar
C-Fan to move the Gas
D-Extractor for the Last of the Tar
E-Naphthalene Extractor
F-Cyanogen Extractor
G-Second Condenser for Benzene Toluene etc.
H-Tower for removing Ammonia by Water
I-Purifier for removing Sulfur Compounds by Ferric Oxide
J-Gas Holder

FIG. 43.

l Gases.—Gaseous fuels f great importance for itic and technical pur- because they are clean very easily controlled. are also finding a rapidly sing use as a source of r in gas engines, so that ibject of fuel gases is one little practical impor- Many different varieties are in use such as natural oal gas, wood gas, oil gas, ie various types of water roducer gases. Natural is already been discussed. and oil gases are of rather d application, so that we levote our attention at oint chiefly to coal, water roducer gas.

l Gas.—Coal gas is made ating bituminous coal in fire clay retorts, Fig. 43. It consists principally of hydro- iethane, unsaturated hydrocarbons and carbon monoxide, heir relative volume is in the order given. In addition to these gases, a large number of valuable by-products dist tar, ammonia, benzene, carbolic acid, etc., and are remc the purification of the gas. Coke is left in the retorts.

Water Gas.—When steam is passed over heated coal o carbon monoxide and hydrogen are formed, if the temp is high,

$$H_2O + C = CO + H_2$$

or carbon dioxide and hydrogen if the temperature is

$$2H_2O + C = CO_2 + H_2$$

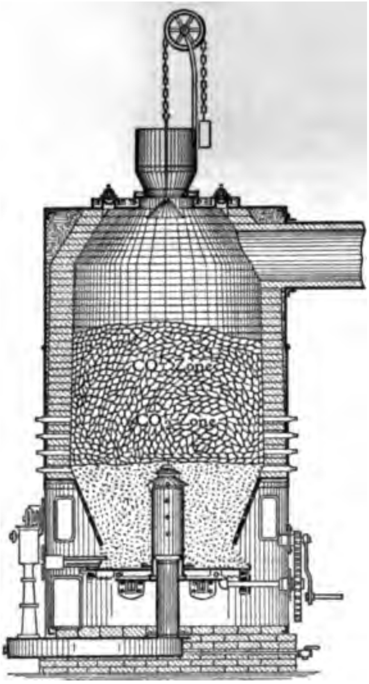


FIG. 44.

The gaseous mixture ob in this way usually runs 50 per cent. hydrogen a per cent. carbon monoxi is very valuable for fu power purposes.

The water gas process great advantage over th coal gas inasmuch as former nearly all of the is converted into gas, w the latter most of it rem coke.

Producer Gas.—Produ is perhaps the most imp fuel gas for industrial and purposes. It is made b slightly different method the first, air is blown up t a deep bed of highly heat in a great stove-like f called a producer (Fig Where the air first ente coal burns to carbon dioxide,

$$C + O_2 = CO_2$$

As the latter is carried up through the bed of carbon, it is r to carbon monoxide,

$$CO_2 + C = 2CO$$

This carbon monoxide mixed with the nitrogen of the air and some unreduced carbon dioxide constitutes the producer gas as made by this method.

The second method is just the same as the first except that some steam is blown in with the air and the reactions are those just given together with the ones for water gas. The reactions for the first method evolve heat, while those for water gas absorb it. By combining the two, a greater amount of the energy of the coal is obtained in the gas than by either alone. The gas made in this way contains carbon monoxide, hydrogen, carbon dioxide, and nitrogen.

A gas engine using producer gas will often deliver one horsepower for an hour, on a pound to a pound and a half of coal used in the producer. The fuel efficiency of such a plant is much greater than that of a steam plant.

Blau Gas.—Blau gas is made by cracking petroleum by heating it to a high temperature then cooling and compressing the products to 100 atmospheres. This liquefies many of the gaseous substances produced. The liquid is sold in strong steel cylinders, which may be connected through reducing valves to the pipes in the building where it is to be used. The blau gas burns with a very bright and hot flame.

FLAMES

Flames are produced by the rapid interaction of two or more gases whereby sufficient heat is generated to render the gases and their products luminous. In most of the cases to which the term is applied, one gas passes in a stream into a larger body of the other and the chemical action takes place at the point of contact of the two.

In the flames with which we are most familiar, the oxygen of the air is one of the active gases and the other is hydrogen, natural gas, coal gas, or some similar mixture; and since the flame is located at the opening whence the gas issues into the air, we very naturally speak of the gas as burning, but the air has just as much to do with the phenomenon as the other gas. As a matter of fact, it is a very easy matter to burn a stream of air in an atmosphere of coal or of natural gas. All that is necessary to do to show this is to place a wide-mouthed bottle, mouth downward (Fig. 45), upon a suitable support, and pass into it a moderate stream of gas until the air is displaced, and then light the gas as it issues from the mouth of the bottle. Now pass a glass tube from which a steady stream of air is escaping up into the bottle. As it goes up through the flame at the mouth of the bottle, the air will take fire, and continue to [illegible]rn in the gas as long as the supply [illegible] two is kept up.

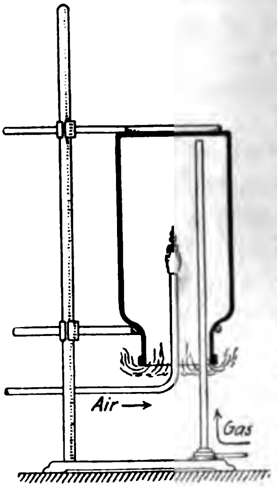


FIG. 45.

All [illegible]es give off light, but they differ enough among themselves so that we may conveniently divide them into two classes; non-luminous and luminous. This classification is arbitrary, because there is every gradation between the typically non-luminous flame of hydrogen and that of acetylene which is the most brilliant of all; that of methane stands near the dividing line.

When infusible non-volatile solids are placed in non-luminous flames, they are heated to incandescence and give out light; a mixture of 99 per cent. thorium oxide, with 1 per cent. cerium oxide, is especially brilliant under these conditions, and it is this mixture which is used in the Welsbach mantles for incandescent gas lighting.

The luminous flames are nearly all produced by the burning of compounds of hydrogen and carbon, and there is much evidence in favor of the view that solid particles of carbon are formed in their interior, and that the greater part of the light is due to the incandescence of these particles. If a cold surface be placed in such a flame, these particles will deposit on it forming a layer of soot or lampblack. In fact, this is the way in which lampblack is made.

If the flame of an ordinary hydrocarbon gas, such as coal gas issuing from a circular opening, be examined, it will be found to consist of a number of conical sheaths or zones fitting one inside the other as indicated in the diagram (Fig. 46). In the relatively luminous sheath "a" water and carbon dioxide are formed, the heat from this radiating inward decomposes the hydro- on toward the base of the flame forming hydrogen and ylene, or hydrogen, methane and acetylene; as gases pass upward the temperature rises and ly reaches a point where the acetylene rapidly mposes into hydrogen and carbon. Since this reaction which takes place with the evolution of , the temperature of the particles of carbon is d even above that of the rest of the flame, and is the cause of the greater part of the light. e changes take place in the zone "b." As the on passes up through the flame, it gradually s, first to the monoxide, then to the dioxide. In nterior of the flame, where the supply of oxygen is limited, arbon is practically all burned to carbon monoxide before ydrogen burns. The luminosity of a flame may be increased utting both gases under greater pressure, or by heating the gas before it leaves the burner. On the other hand, anything which will lower the temperature of the flame will decrease the light. This may be done by holding a cold object in the flame or by mixing some indifferent gas such as nitrogen with the combustible gas. This both dilutes the gas and makes more material to be heated, and hence makes the flame colder.

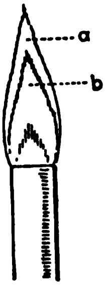


FIG. 46.

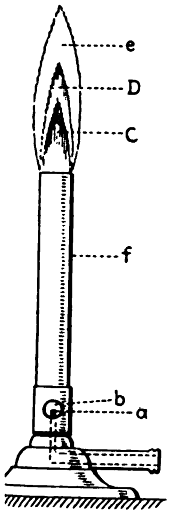


FIG. 47.

Bunsen Burner.—Robert Bunsen, a German chemist, invented the burner which bears his name, in order to burn coal gas with the clean smokeless flame, which is so desirable for chemical purposes. A diagram of the burner and its flame is shown in Fig. 47. The gas enters the burner through the jet "a," and, having a high velocity, it draws a certain quantity of air in at the "b" in the base of the tube "f." In passing up through tube, the gas and the air mix. Three well-marked sheaths rmed in the flame. "C" is non-luminous, and so cold that a match head may be held in it for some time without igniting. In this, practically no chemical change takes place. "D" is bluish-green and very hot, especially at the upper tip, but not very luminous. In it the hydrocarbons are transformed into carbon monoxide and hydrogen. In the outer layer "e" the hydrogen and carbon monoxide burn to water and carbon dioxide. The non-luminous flame of the Bunsen burner is smaller and hotter than a luminous flame burning the gas at the same rate.

CHAPTER XVII

SILICON

General.—Silicon, the second member of the carbon group, curs very abundantly in nature in the form of its oxide and rious silicates. This element, next to oxygen, is present in the rth in the greatest quantity, forming as it does about one-urth of the earth's crust.

Preparation.—Silicon exists in at least two allotropic modifica-ns, one crystalline, the other amorphous. Some evidence o points toward the occurrence of two distinct crystalline rms, corresponding to graphite and diamond.

Amorphous silicon may be prepared by heating finely powdered artz, which is silicon dioxide, SiO_2, with metallic aluminum magnesium; the reaction which takes place with magnesium represented by the following equation,

$$SiO_2 + 2Mg = Si + 2MgO$$

he magnesium oxide is removed by treating the resulting ixture with hydrochloric acid.

Crystalline silicon is now being prepared on a large scale at iagara Falls by reducing the dioxide with carbon in an electric rnace. It is used in the manufacture of steel.

$$SiO_2 + 2C = Si + 2CO$$

alloy of silicon and iron known as ferrosilicon is also used making steel. It is made by heating together sand, iron oxide d carbon in an electric furnace.

Properties.—Amorphous silicon is a dark brown, friable bstance without luster, is a non-conductor of electricity, and s a density of 1.8. If the temperature is raised somewhat it kes fire and burns. The crystalline silicon is very much more sistant chemically and is not attacked by oxygen even at red at. It is dark steel gray in color and forms opaque octahedra ssessing a metallic luster, its density is 2.35.

Both varieties melt at temperatures in the neighborhood of 1,500° to a steel blue liquid which on solidifying always produces the crystalline form. Silicon dissolves in hydroxides of the alkali metals with the evolution of hydrogen and the formation of the corresponding alkali silicates.

$$2NaOH + Si + [illegible] Na_2SiO_3 + 2H_2$$

This reaction is used to make l[illegible]ogen for filling balloons and air ships. Silicon is not solubl[illegible] any single acid but is in a mixture of nitric and hydrofluo[illegible] acids, forming silicon tetrafluoride, and is slowly oxidized by [illegible]qua regia to silicic acid.

Silicon Dioxide.—Silicon forms [illegible]ith oxygen one well-defined compound, silicon dioxide, SiO[illegible]hich is analogous to carbon dioxide. The monoxide, the analogue of carbon monoxide, has been stated to exist and has been described as a brown powder, but as yet this has not been sufficiently confirmed. Silicon dioxide or silica, as it is commonly called, occurs very abundantly on the earth's surface both in the crystalline and the amorphous modifications. The purest form is rock crystal, which is colorless quartz. This compound when colored by different metallic oxides gives rise to smoky quartz and other semi-precious stones. Flint occurs widely distributed in nature, and is rather impure amorphous silica; other forms of this variety are certain kinds of petrified wood, opal and jasper.

On account of its extreme hardness and its transparency, rock crystal finds extensive use in the manufacture of fine lenses. Many laboratory utensils are now made from quartz. When heated before the oxy-hydrogen blowpipe it behaves like glass, in that it becomes pasty and does not pass directly from the solid to the liquid state. In this condition it may be worked and blown into the desired shapes. These vessels are very resistant chemically to nearly all reagents except the alkalies, and consequently they may replace the more expensive platinum in many operations. The temperature coefficient of this fused silica ware is very small, and a crucible heated to redness may be plunged into cold water without being broken.

Silicic Acid and Silicates.—Silicates are known which correspond to an even greater variety of silicic acids than there are sphoric acids. We have for example, salts of orthosilicic acid, SiO_4; meta silicic acid, H_2SiO_3; diortho silicic acid, $H_6Si_2O_7$; ieta silicic acid, $H_2Si_2O_5$; and trisilicic acid, $H_4Si_3O_8$. When oluble silicate is treated with an acid, the solution usually nains clear for a time; and then there is precipitated difficultly uble silicic acid whose composition is rather variable but which ids to approach that of meta silicic acid, H_2SiO_3. When ated, this yields the dioxide and water.

By proper manipulation, a colloidal solution of silicic acid may prepared. A colloidal solution is one which appears perfectly mogeneous to the eye, and which will pass through a filter, ut which has the same boiling- or freezing-point as pure water. Then a beam of very strong light is sent through the solution nd a microscope focused upon its path, a multitude of particles re seen, so extremely minute that they cannot be perceived in ny other way. A true solution is homogeneous even when xamined in this way. This shows that the solute in a colloidal olution is not really in solution, but that it is merely very finely livided and in a state of suspension.

A few of the naturally occurring silicates will be mentioned at this point merely to show how important to us these compounds are. Clay, mica, asbestos, serpentine, and feldspar, are among the principal silicates; while granite (a mixture of quartz, feldspar, nd mica), basalt, prophyry, lava, pumice stone are also common ilicate rocks. Sandstone consists principally of particles of silion dioxide cemented together with calcium carbonate, iron oxide, r amorphous silica from silicic acid.

When exposed to the weather, the silicate rocks are gradually isintegrated under the combined action of water, carbon dioxide, hanges of temperature, freezing and thawing, with the formation f clay (aluminum silicate), silica, and the carbonates of the netallic elements of the silicates. Under proper conditions, these roducts of disintegration will solidify into what are known as the edimentary or secondary rocks, while the original silicates are alled the igneous or primary rocks.

Silicon Hydride.—If in the preparation of silicon by means of metallic magnesium an excess of the metal is used, a compound magnesium silicide, $SiMg_2$, is formed. This compound reacts with hydrochloric acid yielding magnesium chloride and a gas which on contact with the air takes fire spontaneously for smoke rings of silicon dioxide.

$$SiMg_2 + 4HCl = 2MgCl_2 + SiH_4$$

This gas is silicon hydride, SiH_4, the analogue of methane, like phosphine, if carefully purified, loses the property of s taneous inflammability, which property is probably, in this also, due to the presence of some higher hydride.

Halogen Compounds.—If amorphous silicon be treated chlorine, or if a current of chlorine be passed over a mixtu finely powdered quartz and carbon which is strongly heated compound silicon tetrachloride, $SiCl_4$, is formed. Althoug this latter reaction neither the carbon nor the chlorine alo able to effect the decomposition of the silicon dioxide, combined action can bring it about.

$$SiO_2 + 2C + 2Cl_2 = SiCl_4 + 2CO$$

Silicon chloride is a colorless liquid whose boiling-point is It fumes strongly in the air since water readily decompos into silicic acid and hydrogen chloride.

If instead of chlorine, hydrogen chloride is passed over a phous silicon, a compound of the composition $SiHCl_3$ is for and by analogy is called silico-chloroform.

Silicon unites with the other halogens to form similar pounds. The most important of these is the fluoride which gas at ordinary temperatures and is readily formed by trea silica or a silicate with hydrofluoric acid,

$$4HF + SiO_2 = SiF_4 + 2H_2O$$

Silicon fluoride is decomposed by water, hence some dehydr agent such as sulfuric acid must be added to remove that fo in the reaction. Silicon fluoride is most conveniently prep by mixing together silicon dioxide and calcium fluoride, adding concentrated sulfuric acid to the mixture. The rea with water is unlike that of the other halogen compo Instead of silicic acid and hydrogen fluoride, we have complex hydrofluosilicic acid formed according to the equat

$$3SiF_4 + 4H_2O = 2H_2SiF_6 + Si(OH)_4$$

lead salt of this acid is used in the electrolytic purification of l (see p. 417).

arborundum.—Carborundum is the trade name for silicon bide, SiC. It is chemically resistant, so hard it will scratch y, and is used very largely as an abrasive. It is not attacked acids but is gradually decomposed by fused alkalies forming respective carbonate and silicate.

Carborundum is prepared on a large scale at Niagara Falls heating together in an electric furnace (Fig. 48), carbon, nd and sawdust with common salt as a flux. The electric curnt is passed through the carbon core, T (Fig. 48), until the mixure of carbon, sand, etc., has been heated sufficiently. The rnace is then allowed to cool when a cylinder of crystallized rborundum will be found surrounding the carbon core. It then crushed, treated with sulfuric acid to remove impurities ch as iron oxide, washed and graded. The product is then orked up into abrasive wheels, hones and the like. For this irpose the carborundum is mixed with a suitable binding aterial such as china clay and feldspar, molded and baked at a gh temperature.

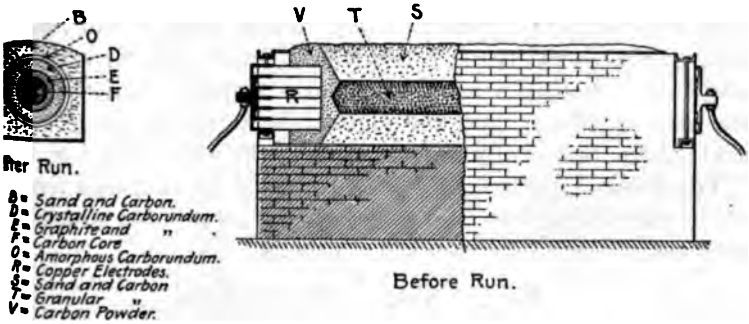


FIG. 48.

CHAPTER XVIII

BORON

General.—Boron is very [illegible] to silicon in properties, both of the free element a[illegible]unds. The formulas of these latter, however, toget[illegible] other considerations connect it quite closely with [illegible] n [illegible]e true metals. It occurs in nature as boric acid, [illegible]alts of this acid, and as the anhydride or boron trioxi[illegible] From these it will be seen that unlike silicon, boron i[illegible]t. The free element may be prepared in both the cr[illegible]d amorphous varieties as in the case of silicon, and the method is much the same as for that substance, viz., by the reduction of the oxide with a metal.

Fused boron has recently been prepared by reducing the trioxide with magnesium, and then heating the product to 2000°–2500° in an electric furnace when it melts.

$$B_2O_3 + 3Mg = 2B + 3MgO$$

The product is black, amorphous and very hard, scratches everything except diamond, but is rather brittle. When cold, it is a very poor conductor of electricity, but at 400° it conducts 2,000,000 times as well as at room temperature. Because of its great temperature coefficient, it is well adapted to the making of devices for the measurement of temperature and for the regulation of electrical machinery.

Boric Acid.—Boric acid, or boracic acid as it is commonly called, is formed by the action of water on the anhydride, boron trioxide. The acid corresponding by analogy to orthophosphoric acid, is H_3BO_3, and is called orthoboric acid. While this acid exists free, nearly all the known salts are formed from acids derived from H_3BO_3 by the loss of water. In nature it occurs as somewhat yellowish scales. It is very soluble in hot water but much less so in cold. The aqueous solution reacts faintly acid.

On being heated, the acid passes first into water and the trioxide, which at a higher temperature melts to a glass-like mass ich is capable of dissolving metallic oxides. Upon this operty depends the use of boric acid as a flux in hard soldering.

While the anhydride is fairly resistant to heat, the acid itself volatile with steam. One of the methods for obtaining the cid depends upon this fact. In the volcanic districts, vapors ontaining boric acid escape from the earth. These are passed nto water, condensed, and the boric acid finally becomes concentrated enough to crystallize out at lower temperatures. When oric acid is introduced into a flame it volatilizes and imparts a reen color to the flame.

Of the many boric acids, we shall mention only the metaboric, formed from H_3BO_3 by the loss of one mole of water, according to the equation, $H_3BO_3 = HBO_2 + H_2O$; and the tetraboric formed according to the equation $4H_3BO_3 = H_2B_4O_7 + 5H_2O$. In any water solution of boric acid, the ions of these different acids exist in equilibrium.

The sodium salt of tetraboric acid, $Na_2B_4O_7 \cdot 10H_2O$ or borax, occurs in California and in others of the western states and is also manufactured by decomposing the naturally occurring calcium borate, $Ca_2B_6O_{11} \cdot 5H_2O$, with sodium carbonate and bicarbonate and recrystallizing. Borax contains either 5 or 10 moles of water of crystallization depending upon the temperature at which it is crystallized. It effloresces in the air and, if heated, swells up, then melts to a glassy substance which dissolves metallic oxides similarly to boric oxide. Some of these solutions have distinctive colors, and are used in blowpipe analysis and in making enamels. Because of the weakness of boric acid a solution of borax is hydrolized enough to be alkaline. On this account it is used to a slight extent in households to soften water, but this is a very costly method. Borax and boric acid have fairly strong antiseptic properties and are used in medicine and as preservatives.

Other Compounds.—The chlorides and other halogen compounds of boron may be prepared in the same way as the corresponding compounds of silicon and are similar in their properties. Since boron is trivalent their general formula is BA_3, where A represents the halogen anion. The fluoride when dissolved in water forms the compound, HBF_4, which is very much like hydrofluosilicic acid in its properties.

Boron readily combines with nitrogen to form boron n
BN, so unless special precaution is taken to exclude the air
the preparation of the free element, the latter is likely to b
taminated with the nitride. This compound is a white p
which when heated with water reacts to form ammonia and
acid,

$$BN + 3H_2O = B(OH)_3 + NH_3$$

CHAPTER XIX

THE ARGON GROUP

The gaseous substances helium, neon, argon, krypton, xenon nd niton form an interesting group of non-metallic elements hich is chiefly remarkable for the fact that no compound of member of this group has ever been prepared. Another ineresting point in connection with these substances is that the lement helium is certainly one of the products of the spontaneous transmutations which the radioactive element radium ndergoes.

The molecular weights of these elements may be easily obained from their gaseous densities but since they will not enter nto combination with any substances, the question as to the umber of atoms per molecule and hence their atomic weight is ot easily answered. But in spite of their inactivity we can rrive at a reasonable conclusion through the following line of rgument.

The quantity of heat necessary to raise the temperature of a ram mole of a substance 1° is called its molecular heat. If the olume is kept constant during the heating, it is known as he molecular heat at constant volume. Now it is an easy matter to determine both the molecular and atomic weights of mercury, and these turn out to be 200 in each case. In addition, the molecular heat at constant volume of mercury vapor is 13 joules. The molecular heat at constant volume of gases having two atoms per molecule such as oxygen, nitrogen, hydrogen, arbon monoxide, etc., lies between 20 and 21 joules, while that or substances having three atoms per molecule is 28 to 33 joules. The molecular heat at constant volume for the members of the rgon group is 12 to 13 joules. We may therefore safely conlude that there is one atom per molecule of these elements just s is the case with mercury, and hence that their atomic and olecular weights are identical.

Helium.—The element helium has an atomic and molecular weight of 4.00. It is found in very small quantites in the air. It is also found in the gases of many mineral springs and is present in relatively large quantities in natural gas. The gas at Dexter, Kansas, contains as high as 1.84 per cent. of helium. Outside of natural gas, the principal source of helium is the rare minerals containing the radioactive elements radium, uranium, thorium, etc., from which it m [illegible] obtained by simply heating the mineral in a vacuum or b[illegible]solving it in dilute sulphuric acid or fused potassium acid [illegible]ate. The helium is simply enclosed in the mineral and is [illegible] in combination. From the fact that it occurs in those min[illegible] which contain radium, etc., it is probable that it is formed i[illegible]e mineral by the transformation of the radioactive element[illegible]he same source is indicated for the helium of natural gas b[illegible]e fact that it contains niton (see p. 265).

Helium was the last gas to be liquefied. This was done in July, 1908, by Kammerlingh Onnes. It is a clear, colorless liquid boiling at – 268.5°C. or 4.5° above absolute zero. Since its critical temperature is – 268.0°C. or + 5° A. it is a very difficult substance to liquefy. When the pressure under which it boiled was reduced to 1 cm. its boiling-point was lowered to 3° above absolute zero. This is probably about the lowest temperature which we will be able to reach unless some more easily volatile liquid than helium is discovered.

Helium under diminished pressure, glows brilliantly upon the passage of an electric discharge. Upon examining the light with a spectroscope the spectrum is found to consist of a number of bright lines, one in the yellow being especially strong (see Frontispiece). Many years before helium was discovered on the earth this line was observed in the spectrum of the sun and ascribed to a then unknown element which was called helium from the Greek name for the sun "helios."

Neon.—Neon has an atomic and molecular weight of 20.2. It is found in the air in slightly larger quantities than helium. It occurs along with helium in the gases of certain mineral springs and in natural gas. Its boiling-point is – 246°. It is easily liquefied in a bulb surrounded by liquid hydrogen which boils at – 253°, and is separated from helium in this way. Neither lium nor neon is absorbed by cocoanut charcoal to any great tent, and a mixture of the two gases may be easily obtained om natural gas by absorbing the other gases in cocoanut char- al cooled with liquid air. Recent experiments indicate that eon may be a mixture of two gases one having an atomic weight 20 and the other of 22.

Argon.—The atomic and molecular weights of argon, are 9.9. It occurs in nature in rather large quantites being pres- nt in the air to the extent of about 1.3 per cent. by weight or .937 per cent. by volume. It boils at − 186° and freezes at - 189°. Argon was the first member of this group to be dis- overed, being found in 1894 in atmospheric nitrogen by Lord ayleigh and Professor Ramsay who were seeking an explana- on for the fact that atmospheric nitrogen was more dense than at from chemical sources. It is separated from nitrogen by mbining the latter with metallic lithium, calcium, or mag- sium at a high temperature, nitrides being formed. It is now ing used in the place of nitrogen in some of the gas-filled tung- en lamps. Its spectrum is shown in the Frontispiece.

Krypton and Xenon.—These gases occur in the air in very small mounts. They are obtained mixed with argon, helium, and eon by the removal of the nitrogen, etc., as indicated above. hey are separated in the pure state by the fractional distilla- ion of the crude argon. Krypton has an atomic and molecular eight of 82.92 and boils at −152°. Xenon has a molecular and tomic weight of 130.2, boils at −109°.

Niton or Radium Emanation.—Radium undergoes a slow pontaneous transmutation and very gradually gives off an inert as of the argon group which is called niton or radium emanation. lthough this is chemically inactive, it is highly radioactive, ee p. 495) and changes into helium and other products at such rate that one-half of it disappears every 3.8 days. Since it is rmed so slowly from radium and decomposes so quickly, there never very much of it available for experimentation at any one me, and Sir William Ramsay who has studied it most fully as displayed great skill in its investigation. It has been shown spite of the fact that it is formed from one element and changes to another, that it is fully entitled to be considered a distinct ement. It has its own characteristic spectrum and set of other properties. Its molecular and atomic weights have been d mined by Ramsay by weighing less than 0.0001 c.c. of the on a balance sensitive to less than $\frac{1}{250,000}$ mgrm. T weights are doubtless identical and are 222.4. It boil −62° and freezes at −71°. Niton is so highly radioactive it shines in the dark, and gives ou comparison with its mass, enorn quantities of heat. When brough contact with chemical compound very frequently decomposes them, will not itself combine with anyth Niton is present in extremely mi quantities in air, soil, rocks, gro water, and the gases that issue from earth. The quantity present in roc proportional to their radium cont and furnishes the easiest method of termining the amount of radium i rock. The rock is dissolved, the ni boiled off and passed into a char gold leaf electroscope (Fig. 49); the quantity of niton and th fore of radium is estimated from the rate at which the gold of the electroscope collapses.

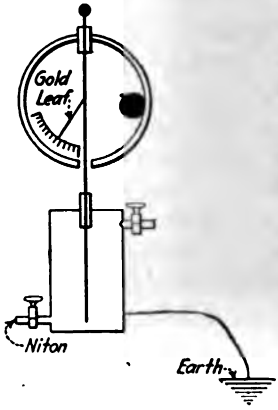


Fig. 49.

The following table giving the per cent. by volume of inert gases in the air is based upon an estimate by Sir Willi Ramsay.

Per Cent. by Volume of Inert Gases in the Air

Helium	0.00040%
Neon	0.00123
Argon	0.9370
Krypton	0.0094
Xenon	0.0011
Niton	Trace.

CHAPTER XX

THE METALLIC ELEMENTS

General.—In the classification of the elements it has been customary for a long time to divide them into the metals and the non-metals. We have been considering the latter in the earlier part of this book, and it now remains to discuss the chemistry of the metals. The division of the elements into these two groups is very convenient, but is entirely arbitrary as is shown by the fact that certain elements have properties in common with each group and cannot be definitively located in either.

Characteristic Physical Properties of Metals.—All metals when not powdered reflect so much of the light which falls upon them that they have an appearance called a metallic luster. Most are silvery white, but a few, such as gold and copper, absorb enough light to show distinct colors. But everything with a metallic luster is not a metal. The non-metal tellurium shows t, as do many compounds, especially the sulfides.

All metals are much better conductors of electricity than electrolytes are, and, unlike the latter, are not decomposed by the passage of the current, hence they are called conductors of the rst class. But several of the non-metals, carbon, boron, selenium, ellurium and many sulfides are also conductors of the first lass.

The metals are better **conductors of heat** than the non-metals, ut in this respect there is not as much difference between the wo groups as in the case of the conduction of electricity.

Most, but not all of the metals, are **malleable** and may be rolled r beaten into thin plates. Gold excels all the others in this espect, and may be beaten into leaves not more than 0.0001 m.m. in thickness.

Most metals are very **tenacious** and will resist a considerable orce tending to pull a given piece apart. This property if associated with the malleability mentioned above renders a metal ductile, so that it may be drawn into wire. Steel is the most tenacious of the metals, and gold the most ductile.

When metals dissolve in most solvents they lose all of their metallic characteristics, and in general form salts, but they may dissolve in one another when fused together and retain the characteristic properties [illegible]s. The solutions of metals in one another are called [illegible]s the term alloy is now used, one or more of the consti[illegible]its [illegible] be a non-metal, but the whole must present the gene[illegible]c properties. Alloys which contain mercury are called an[illegible]ns. Some of these are very important.

Characteristic Chemical P[illegible]ties of Metals.—The most noticeable chemical property [illegible]e metals is that they form simple cations, but this proper[illegible]s not confined exclusively to them; because the non-metals, hydrogen and tellurium also form these ions. Closely connected with the tendency of the metals to form cations is the fact that their hydroxides are generally bases while those of the non-metals are almost invariably acids; but some of the hydroxides of the metals are very weak bases, and a few act both as bases and acids. From the above facts, it may be seen that there is no sharp distinction to be drawn between metals and non-metals, so the division is purely arbitrary; but is nevertheless convenient and practicable because in the great majority of cases no hesitation is felt in making the classification.

Distinction between Metals and Non-metals.—If an element, when in the solid or liquid state, does not have a metallic luster and is not a conductor of electricity, it certainly is a non-metal. If it has the luster and conductivity, it may be either a metal or a non-metal and we must turn to its chemical properties for help in its classification. If it forms simple cations, it is a metal; but if it gives no simple cations and is nearly always found in anions, it is a non-metal. After all aids to classification have been applied, a few elements on the dividing will still be in dispute as to whether they are metals or non-metals, but the great majority will be definitely located.

Classification of the Metals.—A study of the properties of the metals soon shows that they may be divided into groups of more or less closely related elements much as was done with certain the non-metals. The relationship between these elements is rather tangled, however, and some of them have properties which would cause them to be placed in each of several groups and any arrangement which we make of them is more or less arbitrary. There is, however, a natural system for the classification of the elements which is called the periodic system and which includes both the metals and the non-metals. This system is based upon the observation that if the elements be arranged in the order of their atomic weights, similar elements recur at regular intervals; and if the series be broken up into periods such that each period begins with a member of a definite family, the second position in each period will be filled by a member of a closely related group of elements. The same is true for the third and following positions in the series. This may be illustrated as follows; arrange the elements in the order of their atomic weights and we have,

Position,	1,	2,	3,	4,	5,	6,	7,	8
Period No. 1.	He.	Li.	Be.	B.	C.	N.	O.	F.
Period No. 2.	Ne.	Na.	Mg.	Al.	Si.	P.	S.	Cl.
Period No. 3.	A.	K.	Ca.	Sc.	Ti.	V.	Cr.	Mn.

Choosing the members of the helium family as the elements which shall begin our periods, we find that the elements listed here fall into three periods of eight members each, and that the corresponding positions in each period are occupied by analogous elements. We can appreciate this especially for the last four members of the first two periods, since we are familiar enough with the properties of carbon and silicon to see their close relationship and similarly for nitrogen and phosphorus, oxygen and sulfur, fluorine and chlorine. That this same sort of relationship is continued over into the other periods and holds for the remaining positions in these periods, will be evident as we become more familiar with the properties of the elements. For example, lithium, sodium, potassium, etc., which occupy the second positions in the periods, form a part of a group of similar and very closely related metals as we shall soon see. In fact the relationship is fully as close as that between the halogens.

If the elements arranged in series in the order of their atomic weights be broken up into periods in the way given above and these periods be placed vertically under one another, we obtain a table of the periodic classification or system of the ments. Such a table is given below. It is somewhat modification of one prepared by the Russian chemist, Men jeff in 1869, and very similar to a table published in 187 Lothar Meyer, a German chemist, who developed the independently of Mendelejeff.

An inspection of this table will show that chemically si elements are found in vertical columns except in the case o very last group in which the similar elements are found sid side.

In preparing this table, the principle of arrangement in order of atomic weights has been violated in two cases. A with an atomic weight of 39.9 has been placed before potas with an atomic weight of 39.1 and tellurium is put before i although it has the larger atomic weight. The reason fo first change is that potassium does not belong in the group of gases, but in with the other alkali metals in which grou argon would be entirely out of place while it goes very with the other gases of the helium group. Tellurium and io are interchanged because the tellurium evidently belongs t sulfur group and iodine to the halogen. Many researches been undertaken to see if there was not some error in the d mination of the atomic weight of either tellurium or iodin they have led to the conclusion that tellurium actually h higher atomic weight than iodine.

Another defect in the table is that there is no good plac hydrogen. Some have placed it at the head of the hal family and others as the first member of the sodium group. neither these nor any other suggestions which have been m seem to fit the case and the question of the proper locatio hydrogen in the periodic system remains an open one.

There are other imperfections in the table which will bec evident as we go along, but on the whole it furnishes a na and very useful system for the classification of the elements, it seems not unlikely that its apparent irregularities and de will finally be found to have a great significance and to be important.

Although each of the first eight vertical columns in the ta made up of very similar elements, a knowledge of their prope

PERIODIC SYSTEM

		Group 0	Group 1	Group 2	Group 3	Group 4	Group 5	Group 6	Group 7	Group 8
Type Compound			E_2O	EO	E_2O_3	EH_4, EO_2	EH_3, E_2O_5	EH_2, EO_3	EH, E_2O_7	EO_4
Valence		0	+1	+2	+3	−4, +4	−3, +5	−2, +6	−1, +7	+8
Periods	1	He, 4	Li, 7	Be, 9.1	B, 11	C, 12	N, 14	O, 16	F, 19	
	2	Ne, 20.2	Na, 23	Mg, 24.3	Al, 27.1	Si, 28.3	P, 31.0	S, 32.1	Cl, 35.5	
	3	A, 39.9	K, 39.1	Ca, 40.1	Sc, 44.1	Ti, 48.1	V, 51.0	Cr, 52.0	Mn, 54.9	Fe, 55.8; Ni, 58.7; Co, 59
	4	....	Cu, 63.6	Zn, 65.4	Ga, 69.9	Ge, 72.5	As, 75	Se, 79.2	Br, 79.9	
	5	Kr, 82.9	Rb, 85.4	Sr, 87.6	Y, 88.7	Zr, 90.6	Cb, 93.5	Mo, 96.0	....	Ru, 101.7; Rh, 102.9; Pd, 106.7
	6	....	Ag, 107.9	Cd, 112.4	In, 114.8	Sn, 118.7	Sb, 120.2	Te, 127.5	I, 126.9	
	7	X, 130.2	Cs, 132.8	Ba, 137.4	La, 139.0	Ce, 140.3	Nd, 144.3	....	....	
	8	....	....	....	....	....	....	....	....	
	9	....	....	....	Yb, 173.5	....	Ta, 181.5	W, 184	....	Os, 190.9; Ir, 193.1; Pt, 195.2
	10	....	Au, 197.2	Hg, 200.6	Tl, 204.0	Pb, 207.2	Bi, 208	....	....	
	11	Nt, 222.4	....	Ra, 226.0	....	Th, 232.4	....	U, 238.2		

soon shows that each group is composed of two sub-groups, and that the members of each sub-group are found in the alternate rows or periods. This is brought out in the table by setting the rows or periods alternately to the right and left of the group. As a rule, the members of each sub-group are more nearly like one another than they are like the members of the other sub-group within the family. The first member of each group usually has properties in common with both of the sub-groups and forms a connecting link between them.

Group VIII is a rather exceptional group in that it is composed of three sets of elements, each set having three members whose atomic weights, specific gravities and general properties are very similar. In this group, the elements which are most alike are found side by side, although there is also a distinct tendency toward similarity in the vertical columns.

It will be noticed that these sets of three elements come at the end of the third, fifth, and ninth series or periods of the elements

A blank space in the table indicates that no element i known whose atomic weight and properties would give it thi position. It is very probable that some of these elements wil be discovered in the course of time. In the meantime it i possible to make a fairly definite prediction as to the propertie of an element from those of the elements surrounding it in th table. This was done with surprising accuracy by Mendelej for the elements of scandium, gallium, and germanium whic were unknown at the time of the publication of the table.

Not only are the chemical properties of the elements regularl recurrent or periodic functions of the atomic weights, but th same is also probably true of all measurable physical properti with the exception of the specific heat which is inversely propo tional to the atomic weight for all solid elements of a atomic weight higher than 35. This is very clearly shown b Fig. 50 which represents the relation between the density of th elements in the liquid or solid state and the atomic weigh and also that between the absolute temperature of fusion an the atomic weight, the former being shown by the heav lines and the latter by the dotted lines. Most other physic properties yield similar curves and indicate clearly that th properties are periodic functions of the atomic weights.

would be very interesting to know the proportions in which various elements are present in the earth as a whole, but this anifestly impossible since we have no way of getting at the position of its interior. We can, however, get the analysis he air, the ocean, and the rocks composing the outer 10 miles he earth's crust, the lithosphere as it is called, and the follow- table (p. 274) by Clarke of the United States Geological vey gives the results of some thousands of analyses.

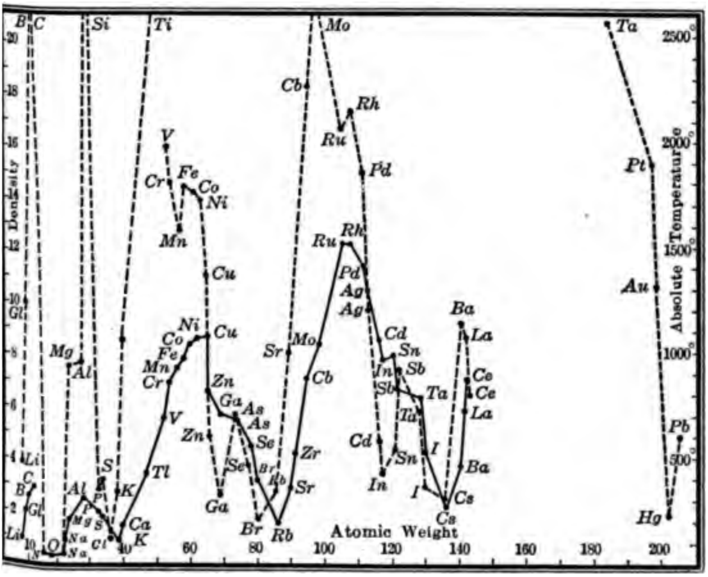


FIG. 50.

All the abundant elements have an atomic weight below 56 d the heavy metals appear to be present in very small quan- ies. The mean density of the earth is about twice that of the osphere and hence it has been supposed that the heavier ele- nts have collected in the interior. Others ascribe the high sity to the compression due to the weight of the overlying ta. This much is certain, however, that the elements cannot be present in equal quantities by weight since their average sity is greater than the mean density of the earth.

Average Composition of Lithosphere, Ocean, and Atmosphere

	Lithosphere (93 per cent.)	Ocean (7 per cent.)	Average including nitrogen
Oxygen	47.33	85.79	50.02
Silicon	27.74	.....	25.80
Aluminum	7.85	.....	7.30
Iron	4.50	.....	4.18
Calcium	3.47	0.05	3.22
Magnesium	2.24	0.14	2.08
Sodium	2.46	1.14	2.36
Potassium	2.46	0.04	2.28
Hydrogen	0.22	10.67	0.95
Titanium	0.46	......	0.43
Carbon	0.19	0.002	0.18
Chlorine	0.06	2.07	0.20
Bromine	.....	0.008	
Phosphorus	0.12	......	0.11
Sulfur	0.12	0.09	0.11
Barium	0.08	......	0.08
Manganese	0.08	......	0.08
Strontium	0.02	......	0.02
Nitrogen	.....	......	0.03
Fluorine	0.10	......	0.10
All other elements	0.50	......	0.47
	100.00	100.00	100.00

CHAPTER XXI

THE ALKALI METALS

$Cs \leftarrow Rb \leftarrow K \leftarrow Li \rightarrow Na \rightarrow Cu \rightarrow Ag \rightarrow Au$[1]

up I of the periodic system is composed of the mono- t alkali metals, lithium, sodium, potassium, rubidium and n, and a distinct sub-group consisting of copper, silver, and The alkali metals resemble one another closely, and may very properly be considered together. In many ts their properties are typical of the metals and a discussion class of elements may profitably begin with them. Cop- ilver, and gold, however, differ so markedly from the alkali s and have so many properties similar to those of metals ging to higher groups, that it seems wise to leave their sion to a later point.

ne of the more prominent properties of the alkali metals are below in tabular form for sake of comparison.

Element	Atomic weight	Density	Melting-point	Boiling-point
n..............	6.94	0.53	186°C.	1,400°C.
n..............	23.00	0.97	97.6°	878°
ium	39.10	0.87	62.5°	758°
ium............	85.45	1.52	38.5°	696°
1..............	132.81	2.40	26.5°	670°

l be noticed that, as the atomic weight increases, the melting- oiling-points decrease and the density increases. Sodium,

ist of the members of each group will be given at the beginning of the ion of the group. To save space, this will be put on one line. The r of the group having the smallest atomic weight, which is also the ting link between the two sub-groups, will be placed about the middle line with the members of the two sub-families at its right or left ac- g as they fall into the right or left hand column in the group in the c system.

however, is somewhat irregular in its density, a fact which may be connected with the position of sodium in the periodic system as the first member of the copper sub-group since these metals all have high densities. This individuality of sodium seems to extend to its chemical properties since potassium, rubidium, and cesium resemble one another much more closely than they do sodium.

The alkali metals are che / the most active of this class of elements and ir ivity as their atomic weight increases. They v pose water, lithium rapidly and cesium with the nce. In each case, hydrogen and the hydroxide is formed. These hydroxides are soluble and are str nd it is this fact that gives to the sub-group the n metals.

None of these ele found free in nature, a fact which might be anticipated from their great chemical activity. Sodium and potassium are among the more common elements and do not differ much in their abundance, but owing to the fact that enormous quantities of sodium chloride have been deposited in the salt beds which are found widely distributed over the earth's surface, while only a few notable deposits of potassium salts are known, the sodium compounds are much more available and consequently much cheaper than the compounds of potassium. Since the sodium salts are fully as good as the potassium for all purposes which do not demand the presence of potassium ion, much larger quantities of the sodium compounds are manufactured and used than of potassium compounds. For this reason, the detailed discussion of the alkali metals will begin with that of sodium.

SODIUM

Occurrence.—Enormous quantities of sodium compounds, chiefly the chloride, are found in sea water, and in places where some of the sea water has been cut off from th and evaporated, great beds of salt have bee supply of this important substance is practic

Other important sodium compounds occur siderable quantities. These are the carbonat arbonate, $NaHCO_3$, the nitrate, $NaNO_3$, cryolite, Na_3AlF_6, rax, $Na_2B_4O_7$, and many of the silicates.

Preparation.—Metallic sodium was first prepared by Davy 1807 by the electrolysis of fused sodium hydroxide, the method iich is used at the present day. Sodium hydroxide is melted an iron vessel (Fig. 51) and electrolyzed between iron or ckel electrodes. Sodium and hydro- n are liberated at the cathode and ygen at the anode; the metallic dium rises to the top of the bath d collects under an iron bell-like ssel from which it is dipped from ne to time. The sodium hydroxide replaced as it is used up, thus king the process continuous. ousands of pounds of sodium are w being made yearly by this process Niagara Falls.

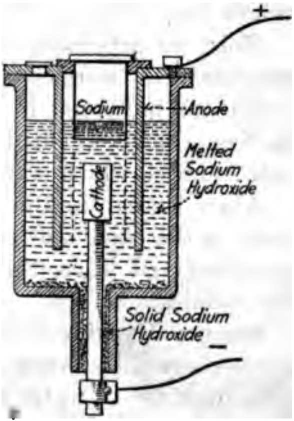


FIG. 51.

Many attempts have been made prepare sodium by the electrolysis fused sodium chloride, but the ap- ratus used has always been so short lived that the processes ve not been successful.

Properties.—Sodium is a soft metal with a brilliant silvery ite luster which is almost instantly lost upon exposure to the owing to the formation of a film of oxide or hydroxide. It lts at 97.6° and boils at 878°. The vapor has a blue color d is exceedingly active chemically. This makes it difficult obtain the molecular weight of sodium, but the results indi- te that its value is 23, the same as the atomic weight. e metal is soluble in mercury, forming sodium amalgam. hen this contains more than a small amount of sodium, it is id. The amalgam is less active chemically than the metal elf, and finds extensive application, because, for many purposes, tallic sodium is too vigorous.

The principal chemical property of sodium is its great tendency pass over into the ionic state. In doing this, the sodium takes positive electricity and hence is a strong reducing agent. Metallic sodium reacts vigorously with water, with the formation of sodium hydroxide and hydrogen. If more than a very small piece of sodium is used, a violent explosion is liable to occur. Ordinarily, the hydrogen evolved does not become sufficiently heated to take fire, but if the motion of the globule of sodium be diminished by placing a piece of filter paper on the surface of the water, the hydrogen catches fire and burns with a yellow flame, the color being due to the sodium.

Moist air acts rapidly upon sodium, but dry air at ordinary temperatures works very slowly. Large quantities of the metal are preserved in soldered tin cans or closely stoppered bottles. Small quantities of the metal are best kept under a petroleum oil which is without action on the metal.

When heated in the air sodium burns with a yellow flame forming the oxide and peroxide. The larger part of the sodium manufactured is used in the preparation of the peroxide and of the cyanide.

Sodium Hydride.—When sodium is heated to 340° in an atmosphere of hydrogen a crystalline compound, NaH, is formed. This dissolves in water with the formation of sodium hydroxide and twice as much hydrogen as an equivalent quantity of the metal. Because of the great amount of hydrogen liberated per unit weight of the substance, it has been proposed to use it as a source of hydrogen for filling balloons. In marked distinction from most of the hydrogen compounds of the non-metals, sodium hydride has no acid properties.

Sodium Chloride.—Sodium chloride or common salt, NaCl, may be prepared by the interaction of moist chlorine and metallic sodium or by neutralizing sodium hydroxide with hydrochloric acid and evaporating.[1]

However, sodium chloride is never manufactured as indicated above, because of the fact that it occurs in nature in large quantities in easily worked beds of salt. From these the salt may be taken by ordinary mining operations when it is known as rock salt; or it may be obtained by boring down into the salt bed and running water down into the boring, allowing it to stand until it is saturated with salt, then forcing or pumping out the brine and evaporating it to secure the salt. Large quantities of salt re obtained by the evaporation of brine from salt springs or from he ocean. Water from the ocean is usually concentrated by xposure to the heat of the sun in shallow basins constructed ear the shore. The salt so obtained is called solar salt. The rincipal impurities contained in salt beds and brines are calcium ulfate and chloride, magnesium chloride and the bromides.

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[1] It is remarkable that dry chlorine will not act on sodium even at the melting-point of the latter.

To remove these, the salt must be purified by crystallization. This cannot be done by preparing a hot saturated solution and llowing it to cool, since the salt is nearly as soluble in cold as in ot water. The salt is purified by boiling the solution which uickly causes the greater part of the calcium sulfate to preipitate, and then concentrating until most of the sodium chloride as crystallized out; but stopping the operation before the other mpurities have begun to separate. Magnesium or calcium hlorides are particularly objectionable, since they cause the alt to deliquesce under ordinary atmospheric conditions. ure sodium chloride will not deliquesce except in the very ampest weather of the summer.

The very pure sodium chloride required for many chemical urposes is obtained by dissolving the salt in water, and saturatng the solution with hydrogen chloride which precipitates out the greater part of the salt. The explanation of this will be given ater.

Aside from its use in food and as a preservative, sodium chloride s the source of practically all other sodium compounds and of the greater part of the chlorine and chlorine compounds of commerce. For these reasons it is a very important substance and s used by the millions of tons yearly.

Sodium Bromide and Iodide.—Sodium bromide and iodide re very similar to the chloride.

The solubility of the bromide is greater than that of the hloride and is in turn exceeded by that of the iodide, so it may e seen that the solubility increases as the atomic weight of the alogen increases.

Both salts are used in medicine and the bromide in photography.

Sodium Oxides.—Sodium monoxide, Na_2O, may be prepared y heating metallic sodium with sodium nitrate or nitrite in the sence of air. The equation for the latter reaction is as follows:

$$2NaNO_2 + 6Na = 4Na_2O + N_2$$

It is a gray substance which reacts violently with water to form the hydroxide NaOH.

When heated in an excess of air to 300°, sodium is oxidized to sodium peroxide, Na_2O_2. To carry out the process, the sodium in thin pieces is placed in aluminum trays which are slowly passed in one direction through an iron tube heated to about 300° while a current of dry air, purified from carbon dioxide, is passed in the opposite direction. [illegible] gs the air from which the oxygen has largely been remo[illegible] ontact with the fresh sodium and so moderates the reac[illegible] ile the nearly oxidized substance comes in contact wit[illegible] sh air and is fully oxidized.

We have here one reacting [illegible] ance moving in one direction and the other in the opposite. [illegible] arrangement is often adopted in chemical work and is [illegible] s "the principle of counter currents." The sodium p[illegible] so prepared finds extensive use as an oxidizing agent and a[illegible] source of oxygen, since it reacts with water with the formation of sodium hydroxide and hydrogen peroxide which then breaks down into water and oxygen. Fused sodium peroxide, known as oxone, is put on the market for this purpose. A small quantity of a copper compound is added to the peroxide to catalytically decompose the hydrogen peroxide.

Sodium Hydroxide.—Sodium hydroxide may be prepared by the action of the metal upon water, and is so prepared when a very pure article is required. The hydroxide obtained by this method is of course too expensive for most purposes, and the bulk of the substance must be prepared in other ways. It may be made in a purely chemical way by adding calcium hydroxide in suspension in water, milk of lime as it is called, to an 8 to 10 per cent. solution of sodium carbonate and boiling for a time. Difficultly soluble calcium carbonate is precipitated and a solution of sodium hydroxide is left:

$$Na_2CO_3 + Ca(OH)_2 = CaCO_3 + 2NaOH$$

Sodium hydroxide is also prepared by the electrolysis of a solution of sodium chloride using mercury for the cathode. Under these conditions, sodium amalgam is formed which is removed from the electrolytic chamber and allowed to react with water when hydrogen and sodium hydroxide will be formed.

he mercury freed from the sodium is returned to the electro- zing chamber and retransformed into the amalgam. At the aphite anodes, chlorine is evolved. This process is carried out Niagara Falls and other places where power is very cheap.

Another successful electrolytic process is that using what is own as the Townsend cell. This is shown in Fig. 52. The ode is graphite; D and D are asbestos diaphragms painted th a mixture of iron oxide, asbestos fiber, d colloidal ferric hydroxide. The thodes are two in number, and are made perforated plates of iron directly in con- ct with the diaphragms. The anode amber is filled with brine which perco- tes slowly through the diaphragms and nks to the bottom of the cathode cham- rs, the remaining space in these cham- rs being filled with kerosene. From ese, the brine passes off through the ose necks, B. When the current is ssed through the cell, chlorine is given f at the anode, and hydrogen and sodium ydroxide appear at the cathode. Since ydroxyl is an anion, it tends to travel ward the anode, but the brine is made to ercolate through the diaphragms rapidly ough to sweep back the hydroxyl and hence prevent what ould otherwise be a serious loss. The cathode solution con- ins both sodium hydroxide and chloride. As this is evapo- ted, the chloride becomes practically insoluble, and may be adily separated from the hydroxide.

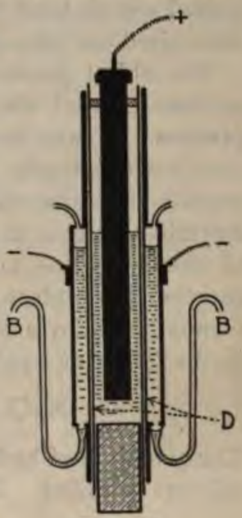

Fig. 52.

Sodium hydroxide is a deliquescent white substance which exceedingly soluble in water. It is a very strong base and is nerally used when such a substance is required as in the manu- cture of soap, paper-pulp, and in many other chemical processes. is also commonly used in the laboratory when a solution ntaining the hydroxyl ion is needed.

Sodium Carbonate.—Sodium carbonate, Na_2CO_3, has so many es that it is almost indispensable to our civilization. It is ind in nature in deposits and in solution in the lakes of the drier parts of the earth's surface. The United States has a number of such lakes, Mono Lake and Owens Lake in California, for example. These two lakes contain over a hundred million tons of the carbonate. It can be extracted cheaply but high transporation charges prevent its general use.

The ashes of sea plants contain sodium carbonate and this was formerly the chief sour [illegible] t. At that time this compound was at least ten [illegible] xpensive than at present and this raised the price of [illegible] ings, notably glass and soap.

The oldest practical [illegible] the preparation of sodium carbonate from the [illegible] t known as the **Le Blanc process.** It was inv [illegible] lanc in 1791. The method involves essentially t [illegible] e first consists in the conversion of sodium chlor [illegible] te, Na_2SO_4, by heating with sulfuric acid in a sh [illegible] pan a mixture of two moles of salt with one mole of "ch [illegible] mber" sulfuric acid. A rapid reaction takes place until half of the salt has been decomposed forming sodium acid sulfate and hydrogen chloride as shown in the following equation:

$$NaCl + H_2SO_4 = NaHSO_4 + HCl$$

The evolution of hydrogen chloride now comes to an end and the mixture solidifies. This mixture is raked out of the pan on to

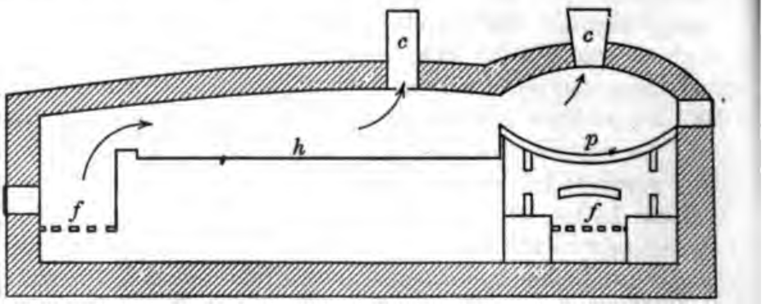

FIG. 53.

the hearth of a reverberatory furnace where it is kept well stirred by rakes and heated to a high temperature by being brought in contact with the flames and hot gases from the fire end of the furnace. Such a furnace together with the decomposing pan is shown diagrammatically in Fig. 53, p is the decomposing pan, h the hearth, f and f the fires and c, c the flues by which the hydrogen chloride and the products of combustion escape.

The furnace is called a reverberatory furnace because the flames are deflected by the roof and caused to play upon the hearth.

On the hearth of this furnace the sodium acid sulfate reacts with the remaining sodium chloride as shown below,

$$NaCl + NaHSO_4 = Na_2SO_4 + HCl$$

The sodium sulfate so obtained is called salt cake.

The second step consists in the reduction of the sodium sulfate to sulfide, Na_2S, by powdered coal; and the third, of the transformation of the sulfide to carbonate by heating with calcium carbonate in the form of chalk, or powdered limestone.

These two reactions are carried out at one operation by heating a proper mixture of sodium sulfate, slack coal and limestone, either in a reverberatory or in a rotary cylindrical furnace through which the flames from the fire box pass. The latter form of furnace saves the great amount of hand labor required to keep the charge stirred on the hearth of the reverberatory furnace. The equations for the reactions are,

$$Na_2SO_4 + 2C = Na_2S + 2CO_2$$
$$Na_2S + CaCO_3 = Na_2CO_3 + CaS$$

The product of this fusion is black in color and is known as black ash. It contains sodium carbonate, calcium sulfide, calcium oxide, coal, and a large number of other susbtances. Sodium carbonate is the only easily soluble substance present hence it is extracted from the black ash by water, using the principle of counter currents by allowing the fresh water to come in contact with the ash from which nearly all the sodium carbonate has been dissolved while the nearly saturated solution acts upon the fresh black ash. In this way, practically all the carbonate is removed from the ash and a nearly saturated solution is obtained. This solution is then evaporated and the salt separates as the monohydrate, $Na_2CO_3 \cdot H_2O$, which is called "crystal carbonate." The crystals are dried at a higher temperature forming the anhydrous salt, Na_2CO_3, known as soda ash. By dissolving this in hot water and allowing it to crystallize at ordinary temperatures, the deca-hydrate, $Na_2CO_3 \cdot 10H_2O$, crystallizes out. This is known as sal soda, or washing soda. It dissolves more rapidly than soda ash and is largely used for domestic purposes, but contains so much water that it does not pay to ship it far.

The sulfur in the c must be recovered for two reasons, first, compet rong in the soda industry and, second, if the su ed to the air and weather it would be gradually dis ate the neighboring streams, and since under the rbon dioxide of the air and water, hydrogen sulfi olved, these streams would be very offensive.

One of the best ways to his sulfur is to suspend the residue in water and pass in carbon dioxide from lime kilns when hydrogen sulfide is formed according to the following equation:

$$CaS + H_2O + CO_2 = CaCO_3 + H_2S$$

This hydrogen sulfide is then burned to water and sulfur in a limited supply of air,

$$2H_2S + O_2 = 2H_2O + 2S \ .$$

The hydrogen chloride evolved in preparing the salt cake is of course saved and either marketed as hydrochloric acid or made into bleaching powder.

The **Solvay** or **ammonia soda process** has been in successful use for more than forty years. It consists essentially in saturating a solution containing sodium chloride and ammonia in the proper proportions with carbon dioxide. When the solutio becomes well saturated, solid sodium bicarbonate, NaHC begins to separate out and continues to do so until a little mo than two-thirds of the sodium chloride has been transformed.

While the mechanical details of the process are so compl that some of the larger works on technical chemistry should b consulted for them, its chemistry is simple. The carbon dioxid ammonia, and water combine to form a solution of ammoniu bicarbonate, NH_4HCO_3,

$$CO_2 + NH_3 + H_2O = NH_4HCO_3 \ .$$

This then reacts with the sodium chloride to form sodium bicarbonate which is precipitated, and ammonium chloride which remains in solution. The equation is,

$$NH_4HCO_3 + NaCl \rightleftarrows NaHCO_3 + NH_4Cl$$

or written in the ionic form

$$NH_4^+ + HCO_3^- + Na^+ + Cl^- \rightleftarrows NaHCO_3 + NH_4^+ + Cl^-$$

The sodium bicarbonate is then filtered off, washed, and heated to change it into the carbonate,

$$2NaHCO_3 = Na_2CO_3 + CO_2 + H_2O$$

The carbon dioxide so obtained furnishes a portion of that required in the process, but the greater part of the gas comes from the burning of limestone in specially designed lime kilns. The ammonium chloride which is left in the solution from which the sodium bicarbonate has separated is worth about eight times as much as the sodium carbonate which it helps to prepare, consequently the ammonia must be recovered and used again. This is done by adding slaked lime to the mother liquor and boiling off the ammonia formed, absorbing it in fresh brine and so keeping it in circulation. The equation is,

$$2NH_4Cl + Ca(OH)_2 = 2NH_3 + 2H_2O + CaCl_2$$

The calcium chloride so obtained is mixed with undecomposed sodium chloride and finds but little application.

The Solvay process produces much purer sodium carbonate than the Le Blanc process and is for many locations the cheaper.

Properties of Sodium Carbonate.—The deca-hydrate forms large transparent crystals which effloresce easily, passing over into the monohydrate. This, in turn, in very dry air or at a higher temperature loses water and becomes anhydrous.

Anhydrous sodium carbonate is a white opaque substance. It dissolves in water with the evolution of heat. A solution of sodium carbonate is fairly alkaline, due to hydrolysis since carbonic acid is a weak acid. For solutions of ordinary concentration, something like 1 to 2 per cent. of the carbonate is hydrolyzed.

Uses of Sodium Carbonate.—Sodium carbonate is used in making glass, soap, in the softening of water, in washing and bleaching of linen and cotton fabrics, washing wool, paper making, dyeing and dye manufacture, the making of sodium salts, as a reagent in the laboratory to furnish the carbonate ion, and for many other important and useful purposes. Its consumption amounts to millions of ton [illegible]

Sodium Bicarbona [illegible] arbonate, $NaHCO_3$, which is also called sodium [illegible] sodium hydrogen carbonate, primary sodium carb [illegible] um carbonate, baking soda, saleratus, or by the house [illegible] soda, occurs in nature along with sodium carbonate. [illegible] ned in the manufacture of sodium carbonate by [illegible] cess or by acting upon the monohydrate with car [illegible]

It is a white cryst [illegible] ich decomposes into sodium carbonate, water, and ca [illegible] when heated to a moderate temperature. A solution of the bicarbonate contains a little carbonic acid formed according to the following equation.

$$2NaHCO_3 \rightleftarrows Na_2CO_3 + H_2CO_3$$

When the solution is boiled, the carbonic acid breaks down into water and carbon dioxide, which escapes in the form of bubbles.

Sodium Nitrate.—Sodium nitrate, $NaNO_3$, occurs widely distributed in nature in small amounts and is found in enormous quantities in certain deposits in the desert regions of Chile. These deposits are scattered over an area a few miles in width and 500 miles long. The crude nitrate always contains considerable sodium chloride, nitrate and perchlorate of potassium, and sodium iodate, with occasionally some chromate. The iodine is an important by-product. The nitrate is purified by dissolving it out of the crude material with hot water and allowing the solution to crystallize.

The yearly production is about 2,000,000 tons which is something like 1 per cent. of the available supply.

Sodium nitrate crystallizes in rhombohedra which melt without decomposition at 317°. It is very soluble in water and deliquesces, which makes it unfit for the better grades of gunpowder. It is used in the manufacture of blasting powder, of nitric and sulfuric acids, of potassium nitrate, as a preservative

: meats, and in making sodium nitrite, but the greater part is ed as a nitrogen fertilizer.

Sodium Nitrite.—Sodium nitrite, $NaNO_2$, is made by heating dium nitrate with lead or iron and recrystallizing the product,

$$NaNO_3 + Pb = NaNO_2 + PbO$$

is very soluble in water though less so than the corresponding tassium salt. It is largely used in the manufacture of organic es.

Sodium Sulfate.—Sodium sulfate, deca-hydrate, $Na_2SO_4 \cdot 10H_2O$ s been known for centuries under the name of Glauber's lts, having been first described by Glauber in 1658. The lt may also be obtained as the hepta-hydrate, $Na_2SO_4 \cdot 7H_2O$ d in the anhydrous state.

As has been mentioned, sodium sulfate is made as the first step the Le Blanc process for the preparation of sodium carbonate d also for use in the manufacture of glass.

The solubility relations between the different forms of sodium lfate are interesting and instructive, being in many ways pical of all salts which crystallize with different numbers of lecules of water of crystallization.

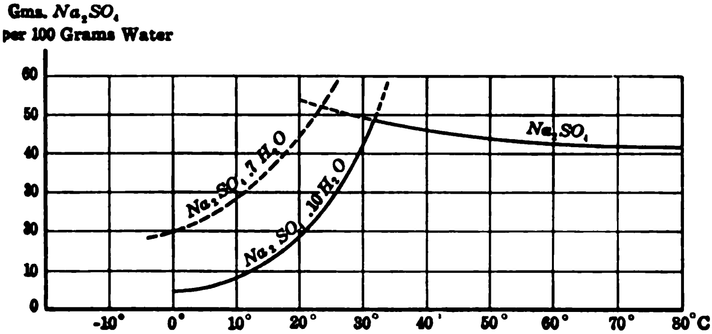

FIG. 54.

The two hydrates and the anhydrous salt are each distinct bstances and as such, each has its own solubility at any given nperature, which, in general, is different from that of either of e others, as is shown by the curves in Fig. 54.

These curves show, for example, that at 20° a solution in equilibrium with $Na_2SO_4 \cdot 10H_2O$ will contain per 100 grm. of water 19.4 grm. of the salt calculated as Na_2SO_4, while those in equilibrium with $Na_2SO_4 \cdot 7H_2O$ or with the anhydrous salt contain respectively 44 grm. and 54 grm. of Na_2SO_4 per 100 grm. of water. These figures demonstrate that the solubility of a salt cannot be expressed by a definite number unless there is given, in addition to the temperat [illegible] pressure at which the measurement is made, the part [illegible] l phase with respect to which the solution is in equilibrium

Sodium sulfate is e [illegible] one to form supersaturated solutions and, if a solution [illegible] pared which is saturated or nearly saturated with the sa [illegible] bout 32°, but which does not contain the smallest trace of [illegible] olid deca-hydrate, be cooled to ordinary temperatures i [illegible] closed with a plug of cotton all the salt will remain in [illegible], although it contains about twice the solute which a saturated solution of the deca-hydrate would contain. If now even a very small piece of a crystal of $Na_2SO_4 \cdot 10H_2O$ be introduced into the liquid, crystallization will at once take place and continue until the solution is no more than saturated. Sodium sulfate is such a common substance that it is almost universally present in dust and the cotton plug is used to exclude the latter, and so prevent the crystallization of the salt.

The solubility curves for the deca-hydrate and the anhydrous salt intersect at 32.4° and hence at this temperature the two salts are in equilibrium and have the same solubility. At all temperatures below this point the anhydrous salt is the more soluble and is meta-stable toward the deca-hydrate, while above this point the deca-hydrate is the more soluble and is meta-stable. In the curves, meta-stable equilibrium is shown by the dotted and the stable by the solid lines.

When crystals of the deca-hydrate are heated to 32.4°, they partially liquefy depositing some anhydrous salt and forming a solution saturated both with the deca-hydrate, and the anhydrous salt. The crystals of the deca-hydrate give a rather high vapor pressure of water and hence effloresce easily upon exposure to the air.

Sodium sulfate is used in medicine as a cathartic and also in the manufacture of glass and of sodium carbonate.

Sodium Sulfite.—Sodium sulfite, $Na_2SO_3 \cdot 7H_2O$, is prepared by viding a solution of sodium carbonate into two equal parts and turating one with sulfur dioxide when carbon dioxide and acid dium sulfite will be formed,

$$Na_2CO_3 + H_2O + 2SO_2 = 2NaHSO_3 + CO_2$$

he remainder of the carbonate solution is then added and carbon ioxide and the neutral sulfite will be produced,

$$Na_2CO_3 + 2NaHSO_3 = 2Na_2SO_3 + H_2O + CO_2$$

In addition to the acid and neutral salts mentioned above, a ompound having the formula, $Na_2S_2O_5$, known as sodium disul-ite or sodium meta-bisulfite is made in rather large quantities or use in photography, as is also the neutral sulfite.

When exposed to the air, the sulfites take up oxygen and are hanged to sulfates. This process is generally retarded by the resence of small quantities of certain organic substances such s alcohol or sugar which here act as negative catalyzers. The se of the sulfites in photography depends largely upon their ower of reacting with oxygen since they are added to the developers," which are strong reducing agents to protect them om the oxidizing action of the air.

Sodium sulfite is also used as an antiseptic or preservative and an "antichlor" to reduce any chlorine which may be left in e goods after bleaching with this substance.

Sodium Sulfide.—Sodium sulfide, Na_2S, is prepared on a large ale by the reduction of the sulfate with powdered coal at a gh temperature as was done in the preparation of sodium car-nate by the Le Blanc process. It dissolves in water and the lution has an alkaline reaction owing to hydrolysis which sults in the formation of some of the hydrosulfide, NaHS, or ther of the hydrosulfide ion, HS^-. The salt crystallizes with ne molecules of water as $Na_2S \cdot 9H_2O$, and is able to take up lfur to form various polysulfides of which the compounds $a_4S_9 \cdot 14H_2O$, and Na_2S_5 are the best known.

Small quantities of these sulfides are used in the laboratory as agents, but the salts find extensive use in the manufacture of me kinds of glass and in the removal of hair from hides.

Sodium Thiosulfate.—Sodium thiosulfate, $Na_2S_2O_3 \cdot 5H_2O$, is an important salt which may be made by boiling a solution of the sulfite with sulfur. The latter is taken up much as oxygen is by the sulfites, and thiosulfates are regarded as sulfates in which one atomic weight of sulfur has taken the place of an atomic weight of oxygen. The salt is obtained as a by-product of the Le Blanc process. The residue of calcium sulfide left in this process slowly oxidizes in [illegible] to the thiosulfate, and when this is treated with sodium car[illegible]ate, calcium carbonate and sodium thiosulfate result.

The penta-hydrate is very [illegible]le and readily forms supersaturated solutions. It melts [illegible]° and if protected from dust will remain liquid at ordinary [illegible]peratures until brought in contact with some of the solid s[illegible] This liquid may be regarded as either the supercooled hydr[illegible] supersaturated solution.

The salt is used as an "antichlor" to destroy the excess of chlorine used in bleaching and as a protection against the "war gas" which is chlorine, and also as a fixing agent in photography, a use which will be discussed in connection with the silver salts.

Oxyhalogen Compounds of Sodium.—The methods of preparation, properties, and uses of sodium hydrochlorite, $NaClO$, and chlorate, $NaClO_3$, have already been given under the oxygen compounds of chlorine and will not be repeated here.

Sodium Phosphates.—Three sodium salts of orthophosphoric acid are known, monosodium phosphate, NaH_2PO_4, disodium phosphate, Na_2HPO_4, and trisodium phosphate, Na_3PO_4. The disodium salt, $Na_2HPO_4 \cdot 12H_2O$, is the most familiar of these. It is made by neutralizing a solution of phosphoric acid with sodium hydroxide or carbonate and allowing it to crystallize. The salt is easily soluble and effloresces readily. It is used in medicine as a laxative and in the laboratory as a soluble phosphate reagent to furnish the hydrophosphate HPO_4^{--}, and the phosphate, PO_4^{---}, ions. Solutions of Na_2HPO_4, are practically neutral in reaction, from which it follows that the ion HPO_4^{--} is but very slightly dissociated into the hydrogen and phosphate ions, so that the concentration of the latter is very small. For this reason, if the solution is to be used as a source of the phosphate ion, PO_4^{---}, sodium or ammonium hydroxide is added to duce the concentration of the hydrogen ion and so make the PO_4^{---} ion break up. The reaction,

$$\underset{c_1}{HPO_4^{--}} \rightleftarrows \underset{c_2}{H^+} + \underset{c_3}{PO_4^{---}}$$

reversible and according to the law of mass action, $c_3c_2/c_1 =$ a nstant. The addition of a base to the solution will decrease e concentration of the hydrogen ion and with it the product of and c_3 and this will of course have to be followed by a decrease c_1, the concentration of the hydrophosphate ion. But the drophosphate ion decreases in concentration by changing into e hydrogen ion, which is used up by the base, and the phosate ion which accumulates in the solution. So a solution of sodium phosphate to which sodium or ammonium hydroxide as been added contains a much larger amount of the phosphate n than a pure solution of the salt and is used when the properes of the phosphate ion are sought.

The trisodium salt, $Na_3PO_4 \cdot 12H_2O$, is made by adding an excess of sodium hydroxide to a solution of the disodium salt and vaporating to crystallization. Its solution in water is very lkaline and the salt is practically completely hydrolyzed into a_2HPO_4 and NaOH. It is used to soften or break "hard ater." It does this by precipitating the calcium and magnesium f the water as phosphates.

The monosodium salt is very soluble in water and the solution s acid toward litmus.

The sodium salts of the other phosphoric acids are not of uch importance, except perhaps the metaphosphate, $NaPO_3$, hich fuses easily and in this state dissolves many oxides and en solidifies to glass-like masses having characteristic colors. or this reason it is used in blowpipe analysis.

Sodium Tetraborate.—Borax or sodium tetraborate, $Na_2B_4O_7 \cdot$ $0H_2O$, has been described under boric acid (see p. 261). Like e metaphosphate, when melted it dissolves metallic oxides, and ves characteristically colored glass-like substances. Because this, it is used in blowpipe analysis. It is also used as a flux in rd soldering.

Sodium Silicate.—A salt having the composition Na_2SiO_3 can made by fusing together sodium carbonate and silicon dioxide.

It is soluble in water and is called water glass. It is used in f proofing wood, in making a kind of artificial stone or sand bri being mixed with sand and lime for this purpose, and in t household for preserving eggs.

Sodium Cyanide.—Sodium cyanide, NaNC, is made on a la scale for use in the extraction of gold, for which purpose it l some advantages over p cyanide; since a given wei of sodium cyanide has in arger amount of cyanogen, essential ion for the purp than the same weight of tassium cyanide. The salt is made by passing ammonia o metallic sodium heated to ° to 400° in an iron vessel w sodium amide, NaN is form l,

$$2Na + \qquad 2NaNH_2 + H_2$$

This sodium amide is th ught in contact with char heated to dull redness when sodium cyanide and hydrogen produced,

$$NaNH_2 + C = NaNC + H_2$$

Sodium cyanide is also made by fusing the mixture of calc cyanamide and carbon obtained by heating calcium cart in an atmosphere of nitrogen with sodium carbonate.

$$Na_2CO_3 + CaCN_2 + C = 2NaNC + CaCO_3$$

Like all other soluble cyanides, sodium cyanide is v poisonous.

Sodium Acetate.—Sodium acetate, $NaC_2H_3O_2 \cdot 3H_2O$, is a v easily soluble salt which is made by neutralizing acetic acid v sodium carbonate. It is used in the laboratory to decrease acidity of a solution without making it neutral or alkaline. ' is useful in analytical chemistry because of the fact that m precipitates will form in weakly acid solutions which are sol in more highly acid solutions. To make the conditions favor for the formation of such a precipitate in a solution which tains a strong acid, such as hydrochloric, all that is necessa to add to the solution sodium acetate in sufficient quan The greater part of the hydrogen ion from the strong combines with the acetate ion to form undissociated acetic a because acetic acid is a weak acid and thus the acidity of solution is decreased.

Analytical Properties of Sodium.—Like the salts of all other tals, the solutions of sodium salts show one set of properties in mmon, and this is really what is meant when it is said that they ntain sodium as ion. In general, the statement of the anatical properties of an ion consists in giving a list of the more mmon ions with which it will form difficultly soluble comunds. There is, however, no very difficultly soluble comund of sodium, so this element must be recognized in some other y. For this, advantage is taken of the fact that the colorless me of the Bunsen burner is colored intensely yellow by very all quantities of sodium and when this flame is viewed through spectroscope, two bright yellow lines are seen if the instrument very powerful or the two may appear as one in the smaller struments (see Frontispiece). This is an exceedingly delicate st and will detect 0.0000000003 grm. of sodium. Enough odium is present in practically all substances to give this test nd one must judge as to whether sodium is present as as inconiderable trace or as an essential constituent from the length f time which the flame color lasts as well as its intensity.

When the light from a powerful arc lamp is examined with a pectroscope a very bright continuous spectrum is seen. If the light from the arc passes through a Bunsen burner flame colored yellow by a sodium compound before it enters the spectroscope, black lines appear in exactly the position of the bright sodium ines when viewed in the absence of the arc light. In fact, the lack lines may be made to change into bright ones simply by iminishing the intensity of the arc. This and other similar xperiments lead to the conclusion that an incandescent gas will ake up from a more intense source of light just that kind of light hich it gives out, and when the more intense source of light is solid, this will produce dark lines on a bright background. The dark lines come just where the incandescent gas alone would give bright lines. The solar spectrum consists of a bright background crossed by a very great number of dark lines many of which are identical in position with bright lines given by terrestrial substances when in the incandescent gaseous state. From hese facts it is supposed that the sun consists of an intensely eated core surrounded by an atmosphere of gases which while ncandescent are much cooler than the core and which contain many of our well-known terrestrial elements. The presence of sodium for example, is clearly indicated by the fact that there are dark lines in the solar spectrum which exactly coincide with the bright lines of the sodium flame (see Frontispiece).

In this way the presence of something like forty terrestrial elements in the sun has been ascertained. Among these may be mentioned hydrogen, h rst discovered in the sun and then found in the earth), c n, carbon, chromium, cobalt, iron, magnesium, maganese, el, silver, sodium, potassium, and vanadium.

UM

Occurrence.—Potassi er found free in nature, but occurs widely distribute quantities in the silicate rocks which compose the greater part of the earth's crust. On an average, potassium constitutes about 2.46 per cent. of the lithosphere. This is the same as the sodium content of the rocks. The silicates when acted upon by water and carbon dioxide slowly decompose and their potassium and sodium content passes into solution. One would expect then that the rivers flowing down into the sea would carry approximately equal quantities of sodium and potassium salts, but this is not the case, since the sodium greatly predominates. The explanation for this is found in the fact that soils have the power to hold back the potassium salts by what is known as adsorption (see p. 228).

Potassium salts are adsorbed by the soils while the sodium salts are not, and hence the latter easily find their way to the ocean. Because of this, the ocean contains relatively more of sodium salts than of potassium (see p. 274).

In spite of this disproportion between the sodium and potassium content of the ocean, it might be expected that the conditions which would give rise to the great deposits of salt would produce smaller deposits of potassium compounds. But since the potassium content of the sea is so small in comparison with that of the sodium, the ancient seas would have had to become nearly completely dry before any potassium salts would be deposited. This would put such salts at the very top of the deposits where they would be extremely liable to be dissolved and shed away. So far as can be reasoned out from our present nditions, such deposits could only be formed when a great body sea water dried up completely in a desert region and the posits became covered so deep by dirt blown in from the surundings that they were protected from any further action of ater. At any rate the condition would be quite exceptional, d as a matter of fact only three large deposits of potassium lts are known; that in the neighborhood of Stassfurt, Germany, smaller one at Kalusz in Austria, and another in northeastern pain near Barcelona. The climate of these regions is now far om that of a desert, but there is some evidence that it was such the time of the formation of the deposits. The discovery of ds of potassium salts in this country has frequently been ported of late, one of the most promising being that at Searles ke in California and another the deposits of basic alum called unite in Utah.

Potassium Compounds and Plants.—Growing plants seem to ve an imperative need for compounds of the alkali metals, tassium and sodium. Those which grow on the land take up tassium compounds from the soil to such an extent that their hes formerly constituted the chief source of these compounds. e plants growing in the sea and many of those along the seaore are rich in sodium salts. Some sea plants, however, tably the giant kelps of the Pacific, take up potassium comunds in such quantities that they may become an important tor in meeting the needs of this country for these very imrtant substances. Large plants for the commercial extraction potash salts from kelp are now being put in operation.

There is then a direct connection between the soluble potassium ntent of a soil and its fertility, for, of course, plants can only d upon soluble substances. The soils usually contain large nounts of insoluble potassium compounds chiefly silicates, ich slowly decompose under the action of the water and carbon oxide, giving rise to soluble potassium salts and thus tending keep up the supply of the latter in the soil. But if the land kept under cultivation and the greater part of the crop removed is often the case, soluble potassium compounds cannot be rmed as rapidly as they are needed, and the fertility of the soil ust decrease. The remedy is obviously to restore everything possible to the soil, and to make up the deficiency in potassium by use of some of the potassium salts as fertilizers.

Animals have need for considerable quantities of sodium compounds chiefly for the chloride which constitutes the greater part of the salts in the body fluids, but their demand for potassium is rather small. Herbivorous animals get with their food much larger quantities of potassium and smaller quantities of sodium than they need. Now the tion of the unnecessary potassium seems to be unavoida ccompanied by the excretion of the useful sodium compound and this accounts for the great appetite for sodium chlorid own by herbivorous animals. Carnivorous animals get their and potassium in the proper proportions in their food an o not care especially for salt.

Preparation of the etallic potassium was first prepared by Davy 180 le by the same method that was used in the preparation of sodium, the electrolysis of the fused hydroxide. The demand for potassium is not large and only small quantities are made, because sodium which is much cheaper, will do nearly everything that potassium can do, and since the atomic weight of potassium is 39.1 while that of sodium is 23, 39.1 parts of potassium would be required to do the work which would be done by 23 parts of sodium at a much lower cost.

Physical Properties.—Potassium is a silver white metal which very quickly tarnishes upon exposure to moist air. It is waxy at ordinary temperatures, melts at 62.5° and boils at 758°; the vapor is blue in color and the molecular weight is apparently identical with the atomic weight, 39.1. Potassium easily forms an alloy with mercury which is much like the corresponding sodium amalgam.

Sodium and potassium form an alloy which is interesting because, if it does not contain too much sodium, it is a liquid at ordinary temperatures.

Chemical Properties.—The chemical properties of potassium are practically the same as those of sodium except that potassium is somewhat more active, so that when thrown upon water the potassium gets hot enough to set fire to the hydrogen which is evolved and which burns with a violet flame, this being the color given to flames by potassium compounds.

In fact, the entire chemistry of m is so similar to that sodium that in most cases it will be necessary to add to what s given under sodium merely the slight points of difference esented by the potassium compounds.

Potassium Hydride.—Potassium hydride, KH, is prepared in e same way as the sodium hydride and is very similar to it in its operties.

Potassium Oxides.—Potassium forms two compounds with ygen, a monoxide, K_2O, which dissolves in water to give otassium hydroxide and a peroxide, K_2O_4, which differs from e peroxide of sodium in composition, but like it, dissolves in ater with the formation of the hydroxide, hydrogen peroxide nd oxygen.

Potassium Hydroxide.—Potassium hydroxide, KOH, or caustic potash is so similar to sodium hydroxide that practically verything which was said concerning that compound might be epeated here as a description of potassium hydroxide. It may e prepared by the electrolysis of potassium chloride or by acting pon a dilute boiling solution of the carbonate with calcium ydroxide (milk of lime), calcium carbonate being precipitated nd potassium hydroxide left in solution. It is exceedingly oluble.

It is a very strong base and is used as such, but wherever possible odium hydroxide is used in its place. The reason for this is hat the sodium hydroxide is cheaper and less of it is required to o a given amount of chemical work because of the smaller tomic weight of sodium.

Potassium hydroxide is very deliquescent, and its solutions ake carbon dioxide from the air forming the carbonate which is lso deliquescent.

The chief technical use for potassium hydroxide is in the manuacture of soft soap and of oxalic acid.

Potassium Chloride.—Potassium chloride, KCl, is found in the otassium deposits of Stassfurt and is known as sylvite. It is lso found there as double salts with magnesium chloride, $Cl{\cdot}MgCl_2{\cdot}6H_2O$, known as carnallite and with magnesium sulte, $MgSO_4{\cdot}KCl{\cdot}3H_2O$, kainite. The greater part of the potasum chloride of commerce is made from carnallite. The crude rnallite is crushed and heated with a solution of magnesium loride left from previous operations. In this the carnallite possible to the soil, and to make up the deficiency in potassium by use of some of the potassium salts as fertilizers.

Animals have need for considerable quantities of sodium compounds chiefly for the chloride which constitutes the greater part of the salts in the body fluids, but their demand for potassium is rather small. Herbivorous animals get with their food much larger quantities of potassium and smaller quantities of sodium than they need. Now the [illegible] tion of the unnecessary potassium seems to be unavoida[illegible] companied by the excretion of the useful sodium compou[illegible] and this accounts for the great appetite for sodium chlorid[illegible] own by herbivorous animals. Carnivorous animals get their s[illegible] and potassium in the proper proportions in their food and h[illegible] o not care especially for salt.

Preparation of the [illegible] letallic potassium was first prepared by Davy 180[illegible] le by the same method that was used in the prepara[illegible] lium, the electrolysis of the fused hydroxide. The demand for potassium is not large and only small quantities are made, because sodium which is much cheaper, will do nearly everything that potassium can do, and since the atomic weight of potassium is 39.1 while that of sodium is 23, 39.1 parts of potassium would be required to do the work which would be done by 23 parts of sodium at a much lower cost.

Physical Properties.—Potassium is a silver white metal which very quickly tarnishes upon exposure to moist air. It is waxy at ordinary temperatures, melts at 62.5° and boils at 758°; the vapor is blue in color and the molecular weight is apparently identical with the atomic weight, 39.1. Potassium easily forms an alloy with mercury which is much like the corresponding sodium amalgam.

Sodium and potassium form an alloy which is interesting because, if it does not contain too much sodium, it is a liquid at ordinary temperatures.

Chemical Properties.—The chemical properties of potassium are practically the same as those of sodium except that potassium is somewhat more active, so that when thrown upon water the potassium gets hot enough to set fire to the hydrogen which is evolved and which burns with a violet flame, this being the color given to flames by potassium compounds.

In fact, the entire chemistry of potassium is so similar to that sodium that in most cases it will be necessary to add to what s given under sodium merely the slight points of difference esented by the potassium compounds.

Potassium Hydride.—Potassium hydride, KH, is prepared in e same way as the sodium hydride and is very similar to it in its operties.

Potassium Oxides.—Potassium forms two compounds with ygen, a monoxide, K_2O, which dissolves in water to give tassium hydroxide and a peroxide, K_2O_4, which differs from e peroxide of sodium in composition, but like it, dissolves in ater with the formation of the hydroxide, hydrogen peroxide nd oxygen.

Potassium Hydroxide.—Potassium hydroxide, KOH, or caus-ic potash is so similar to sodium hydroxide that practically verything which was said concerning that compound might be epeated here as a description of potassium hydroxide. It may e prepared by the electrolysis of potassium chloride or by acting pon a dilute boiling solution of the carbonate with calcium ydroxide (milk of lime), calcium carbonate being precipitated nd potassium hydroxide left in solution. It is exceedingly oluble.

It is a very strong base and is used as such, but wherever possible odium hydroxide is used in its place. The reason for this is hat the sodium hydroxide is cheaper and less of it is required to o a given amount of chemical work because of the smaller tomic weight of sodium.

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Potassium nitrate is used in the laboratory, in medicine, in preserving meats to which it imparts a red color, and in the manufacture of fireworks and gunpowder. This last use absorbs by far the greater part of the KNO f commerce.

The composition of gunpowd aries somewhat but is near 75 per cent. potassium nitrate, 1 er cent. sulfur, 14 per cent.

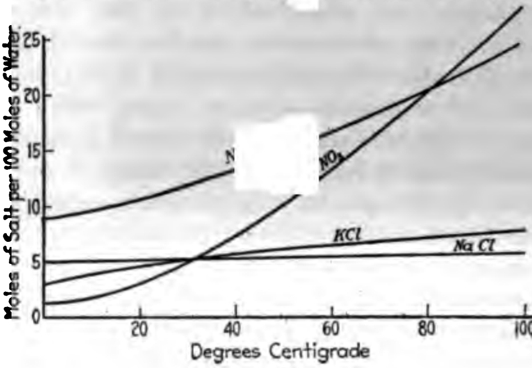

Fig. 55.

charcoal, and 1 per cent. water. The solid ingredients are pulverized separately, mixed together, moistened and ground until thoroughly incorporated. The mixture is then subjected to great pressure and afterward broken up into fragments which are sorted into sizes by sifting. The grains are polished or given a glaze by rattling them in a barrel, dried to remove the water added during the various operations, and finally dusted by passing the powder over very fine sieves.

Gunpowder contains two easily combustible substances, sulfur and charcoal in intimate contact with a very good oxidizing agent, potassium nitrate. At a somewhat elevated temperature, these react very rapidly with the production of the gases nitrogen, carbon monoxide, carbon dioxide, hydrogen, marsh gas, hydrogen sulfide and a number of solid substances chief among which is potassium carbonate. The great amount of gas produced together with the high temperature of the reaction, about 2,200°C., produces great pressure which would reach above 6,400 nospheres or 47 tons per square inch if the products of the plosion occupied the volume of the gunpowder before the plosion. To this high pressure the well-known effects of npowder are due.

Sodium nitrate is much cheaper than the potassium salt, and used in making the lower grades of powder for blasting, but nnot be used in the better kinds because it is deliquescent.

Potassium Carbonate.—Potassium carbonate, K_2CO_3, which is lled potash or pearlash was formerly the most important of the tassium salts as it was the source of other potassium comunds, but since the discovery of the Stassfurt deposits it has rgely lost its position. In former times, it was obtained from ood ashes by leaching them, using the principle of counter rrents, but it is now chiefly obtained from the potassium sulfate the Stassfurt deposits by a modification of the Le Blanc ocess for the preparation of soda; or from potassium chloride taking advantage of the fact that when carbon dioxide under essure is passed into potassium chloride solution containing agnesium carbonate in suspension, a double salt having the rmula $KHCO_3 \cdot MgCO_3 \cdot 4H_2O$ is deposited at temperatures low 24°C. This salt is decomposed by hot water, forming gCO_3 which is precipitated, carbon dioxide which passes out of e solution, and a solution of potassium carbonate from which e salt may be obtained.

Potassium carbonate is also obtained from the residue of beet gar manufacture, and some is still extracted from wood ashes.

Potassium carbonate is a white solid; it is deliquescent and ence is very soluble in water. The solution is alkaline in action because of hydrolysis and the formation of $HCO_3^- +$; H^-.

It is used in making soft soaps, hard glass, and for the preparaon of other potassium salts.

Potassium Bicarbonate.—Potassium bicarbonate, $KHCO_3$, tassium acid carbonate or primary potassium carbonate as it called, like the corresponding sodium compound, is much less luble than the normal carbonate and may be prepared by ssing carbon dioxide through a strong solution of the carbonate.

Potassium Cyanide.—Potassium cyanide, KNC, is an imrtant salt which is manufactured by heating potassium ferrocyanide, $K_4Fe(NC)_6$, with potassium carbonate when the following reaction takes place,

$$K_4Fe(NC)_6 + K_2CO_3 = 5KNC + KNCO + CO_2 + Fe$$

The salt KNCO is potassium cyanate and cannot be easily separated from the cyanide. If the ferrocyanide is heated alone, carbide of iron and nitrogen [illegible]rmed besides the potassium cyanide. This process gives [illegible] KNC but wastes cyanogen. By heating a mixture of dry po[illegible]m ferrocyanide with sodium, a mixture of potassium and so[illegible] cyanides is obtained which is as good for most purposes as [illegible]ssium cyanide and is sold as such. The equation is,

$$K_4Fe(NC)_6 + 2Na = \text{[illegible]}C + 2NaNC + Fe$$

Potassium cyanide is now made by the action of ammonia upon a fused mixture of potassium carbonate and charcoal. The reaction is apparently much like that for the preparation of sodium cyanide from the metal, ammonia and charcoal; for metallic potassium may be formed by the action of carbon on the carbonate.

Potassium cyanide is very soluble in water and the solution is intensely and very rapidly poisonous. Hydrocyanic acid is a very weak acid, so solutions of potassium cyanide react alkaline owing to hydrolysis. The hydrocyanic acid formed can be readily detected by its odor.

Potassium cyanide is used in large quantities in gold mining and in electroplating with gold and silver. It is used in the laboratory wherever a solution containing the cyanogen ion is required and also as a reducing agent. When it acts in the latter capacity, potassium cyanate KNCO is formed. When heated with sulfur, the latter is taken up forming a thio compound analogous to the cyanates, known as potassium thiocyanate, KNCS, which is used in analytical work. This salt is sometimes, though incorrectly, called potassium sulphocyanide.

Potassium Sulfate.—Potassium sulfate occurs in nature in schoenite $MgSO_4 \cdot K_2SO_4 \cdot 6H_2O$ and several other Stassfurt salts. It is obtained from schoenite by adding potassium chloride and a little water, on heating, the comparatively difficultly soluble ıssium sulfate crystallizes out and magnesium chloride is left ɔlution.

; is used in the preparation of potassium carbonate and of n, $KAl(SO_4)_2 \cdot 12H_2O$ but chiefly as a fertilizer.

nalytical Properties of Potassium.—Solutions of potassium all have certain properties in common which are expressed saying that they contain potassium as ion.

'otassium compounds impart to the flame of the Bunsen burner a et coloration which is easily masked by a little sodium unless flame is viewed through a blue glass which cuts off the yellow um light and allows the violet of the potassium to be seen. spectrum of potassium consists of a fairly strong line toward extreme red end of the spectrum, a much fainter red line near orange and a weak line well out in the violet end of the specn. In between these lines is a host of faint ones so close ther that in the smaller instruments they are not seen ırately, but appear as a band of light from the orange to the et (see Frontispiece). None of the potassium lines is anyre near as intense as the sodium line and hence the spectroɔic test for potassium is far less delicate than that for sodium. otassium in the ionic condition differs from sodium in that it combine with a number of different ions to form compounds ch are sufficiently difficultly soluble in water to make them ful for the detection and determination of this element. urally for such a purpose the less soluble a salt the more ful it is, since the delicacy of the test and the accuracy of the ermination depend directly upon this property.

'otassium cobaltinitrite, $K_3Co(NO_2)_6$, is the least soluble he potassium salts, and is thrown down as a yellow precipie when a solution of sodium cobaltinitrite, $Na_3Co(NO_2)_6$, ich contains the cobaltinitrite ion $Co(NO_2)_6{}^{---}$ is added to eutral or slightly acid solution of a potassium salt, unless the er be very dilute. This is a sensitive test for potassium, is not as characteristic as the spectrum since ammonium, idium, and cesium compounds give very similar precipitates h the cobaltinitrite. But ammonium compounds are easily ıoved and rubidium and cesium occur so rarely that practically test is a very good one for potassium.

'otassium cobaltinitrite has a small but definite solubility which is diminished by the presence of an excess of either potassium or of cobaltinitrite as ion. In fact, it is a general rule that the solubility of a salt is diminished by increasing the concentration of one of its component ions.

Potassium as ion will also give rather difficultly soluble precipitates with picric acid, $C_6H_2(NO_2)_3OH$, perchloric acid, $HClO_4$, hydrofluosilicic acid, [illegible] chloroplatinic acid, H_2PtCl_6, and tartaric acid, $H_2C_4H_4$[illegible] precipitates being potassium picrate, $C_6H_2(NO_2)_3OK$, p[illegible] perchlorate $KClO_4$, potassium fluosilicate, K_2SiF_6, [illegible]tassium hydrogen tartrate $KHC_4H_4O_6$. The conditions [illegible] affect the solubility of this latter compound are so typical [illegible]ose of other compounds that they are worthy of a careful study.

When a strong solution of [illegible]ic acid is added to a rather concentrated solution of a p[illegible]um salt, say the chloride or nitrate, the solution becomes supersaturated with respect to potassium hydrogen tartrate, $KHC_4H_4O_6$. This supersaturation may be so great that the solution will spontaneously deposit crystals, or it may persist until the solution is shaken vigorously or until a minute crystal of the salt is added. Of course after crystallization has once started it will continue until the solution becomes exactly saturated with the salt. After this point has been reached the addition of various reagents will produce interesting changes in the solubility of the substance. For example, the addition of a few drops of sodium hydroxide solution will cause a marked increase in the quantity of precipitate showing that the solubility of the potassium hydrogen tartrate has been decreased, but the addition of an excess of sodium hydroxide will cause the entire precipitate to disappear showing that an excess of this reagent increases the solubility of the potassium salt.

Further, the addition of either sodium acetate or of a very soluble potassium salt will decrease the solubility of the hydrogen tartrate, and cause a marked increase in the quantity of precipitate formed in the solution described above.

The addition of a very moderate amount of one of the strong acids such as hydrochloric, nitric, or sulfuric to a solution containing a precipitate of potassium hydrogen tartrate will increase the solubility of the latter and cause the precipitate to disappear.

Acetic acid on the other hand has but little effect. Tartaric acid is a weak acid and this behavior of its potassium salt is typical of all difficultly soluble salts of weak acids, so that a general law may be put forward which says: *The difficultly soluble salts of weak acids dissolve upon the addition of stronger acids.* The converse of this is not true, the difficultly soluble salts of strong acids are not dissolved by weak acids nor are they, as a rule, dissolved by strong acids.

Various more or less satisfactory explanations for these phenomena may be given, but the most useful and instructive is that offered by a combination of the theory of electrolytic dissociation with the law of mass action. According to the theory, an electrolyte in solution is partially broken up into ions as shown below for acetic acid,

$$\underset{c_1}{HC_2H_3O_2} \rightleftarrows \underset{c_2}{H^+} + \underset{c_3}{C_2H_3O_2^-}$$

This is to be regarded as a reversible reaction and so subject to the law of mass action. Hence if c_1 represents the concentration of the undissociated acetic acid and c_2 and c_3 that of the hydrogen and acetate ions respectively, equilibrium will result when,

$$\frac{c_2c_3}{c_1} = K$$

If this be tested by experiment, the various concentrations being calculated from the electrical conductivity of the solution, the result will be found to agree closely with the theory as expressed in the mathematical relation just given. This is true not only for acetic acid but also for all other weak acids and for weak bases. It is true too, for dilute solutions of the more highly dissociated substances, the strong acids and bases and the salts, but apparently does not hold for the more concentrated solutions of these substances. This may be due to the conductivity being an imperfect measure of the concentration of the ions in such solutions, or to some other influence being superimposed upon those which are measured. Fairly satisfactory explanations of these deviations can be given, but are not of interest at this point because these deviations from the simple theory and law given above are not such as would alter any conclusion which we might reach as to the kind of change which would follow the addition of any given reagent, but would simply affect the calculation as to the extent of such change. For qualitative purposes, then, the theory of electrolytic dissociation and the law of mass action may be combined and treated as though they exactly describe the actions of the substances. With this as preliminary, the discussion of the action of the various reagents upon potassium hydrogen tartrate as precipitated from solutions of potassium nitrate by solution of tartaric acid may be taken up in detail. The equation for the main reaction and equilibrium is as follows:

$$\underset{c_1}{K^+} + NO_3^- + H^+ + \underset{c_2}{HC_4H_4O_6^-} \rightleftarrows \underset{c_3}{KHC_4H_4O_6} + H^+ + NO_3^- \quad \text{(I)}$$

The eqilibrium here is between the potassium ion, the hydrogen tartrate ion, and the undissociated potassium hydrogen tartrate. The concentration of these substances being represented respectively by c_1, c_2, and c_3, the mass law equation becomes,

$$\frac{c_3}{c_1c_2} = K$$

It cannot be too strongly emphasized that c_3 represents the concentration of that portion of the potassium hydrogen tartrate which, while undissociated, is actually present in the solution in the dissolved state. It does not in any way represent that which is present as a precipitate. The only connection between c_3 and the precipitate is found in this, that when the solution is in equilibrium with some of the precipitate, *i.e.*, is saturated, the equilibrium will be between the undissociated $KHC_4H_4O_6$ in solution and that in the precipitate; and in this case, as in all others where there is equilibrium between the same substance in two phases, the equilibrium is determined by the ratio of the concentration of the substance in the two phases and not by the absolute amount of either phase. Therefore, since the concentration of the $KHC_4H_4O_6$ is fixed and constant in the solid phase, c_3, that of this substance in solution must be fixed and constant also. From which it would follow that the product of c_1 times c_2 would be constant for this saturated solution, and this point should be appreciated and kept thoroughly in mind.

In addition to equilibrium I, given above, there are two others hich are of importance in this connection.

$$\underset{c_4}{H^+} + \underset{c_2}{HC_4H_4O_6^-} \rightleftarrows \underset{c_5}{H_2C_4H_4O_6} \qquad \text{(II)}$$

he condition for equilibrium being, $\frac{c_5}{c_4c_2} = K'$

d

$$\underset{c_4}{H^+} + \underset{c_6}{C_4H_4O_6^{--}} \rightleftarrows \underset{c_2}{HC_4H_4O_6^-} \qquad \text{(III)}$$

quilibrium resulting when, $\frac{c_2}{c_4c_6} = K''$

ow it must be remembered that all three of these equilibria are resent at the same time in a solution which contains potassium itrate and tartaric acid, and that anything which alters one hanges each of the others.

The addition of a few drops of sodium hydroxide to the solution will affect first equation II by decreasing c_4, the concentration of the hydrogen ion, through the formation of water, but a ecrease in c_4 will be followed by a decrease in c_5 and this will esult in an increase in c_2. But c_2 comes in the equilibrium I nd its increase at once produces an increase in c_3. However, he solution was saturated with potassium hydrogen tartrate nd hence the increase in c_3 makes it supersaturated and results in the increase in the precipitate mentioned in the list of acts which were to be explained.

The action of sodium acetate can now be easily understood ince it acts like the hydroxide to decrease the concentration of he hydrogen as ion.

An excess of sodium hydroxide, it will be recalled, redissolved he precipitate of potassium hydrogen tartrate; the explanation or this apparently contradictory behavior is as follows: As the ydroxide is added, water is formed decreasing c_4 and causing the ndissociated tartaric acid to break up as shown in II until all the artaric acid is transformed then the further addition of hydroxde will result in the breaking up of the hydrotartrate $HC_4H_4O_6^-$ s shown in equation III; so by decreasing c_4 through the addiion of NaOH, c_2 will be first increased and then decreased. But

since c_2 is one of the factors in equation I, a decrease in c_2 will affect I, and will have to be followed by a decrease in c_3. But if c_3 is decreased, the solution will become unsaturated and some of the precipitated substance will have to go into solution. So it may be easily seen why the solubility of potassium hydrogen tartrate is increased by the addition of an excess of sodium hydroxide.

The increase in solubility of K $C_4H_4O_6$ upon the addition of strong acids can be easily explained by considering the effect of the increase in the concentration of the hydrogen ion, c_4, upon II. If c_4 is increased, to keep the fraction c_5/c_4c_2 constant, c_5 will have to increase which can only happen at the expense of c_2, so c_2 will decrease. But in I a decrease in c_2, as we have seen, is followed by a decrease in c_3 and this in turn by the solution of the precipitate. The failure of acetic acid to redissolve the precipitate can be understood, because acetic acid is so weak that it does not materially increase c_4 and therfore does not decrease c_2 and c_3, and hence leaves the solubility practically unaltered.

While potassium hydrogen tartrate is a fairly important substance, great quantities of it being used in the more expensive baking powders for example, it is not important enough to justify the time expended upon this discussion were it not for the fact that it is typical of most other substances, and that a thorough understanding of what is going on here will enable the student to deal easily with all other cases.

Under sodium chloride it was mentioned that this salt would be precipitated from its saturated solution by the addition of hydrogen chloride.

This may be understood by considering the following equilibrium:

$$\underset{c_1}{Na^+} + \underset{c_2}{Cl^-} \rightleftarrows \underset{c_3}{NaCl}$$

$$\frac{c_3}{c_1c_2} = K$$

If now hydrogen chloride be passed into the solution, c_2 will be increased, and this will of necessity be followed by an increase in c_3, and a decrease in c_1 to correspond; but an increase in c_3 makes the solution supersaturated, and brings about the precipitation of the salt. A strong solution of hydrochloric acid may be used tead of the gaseous hydrogen chloride with similar results. tassium chloride will be precipitated in the same way and for e same reason by passing hydrogen chloride into its solution.

As was mentioned in the preliminary to this discussion, page 305, s simple form of mass law treatment does not take into account the factors and hence does not quantitatively describe the mplex phenomena present in these cases, but it does fit them d others qualitatively.

Rubidium and Cesium

The methods of spectroscopic analysis were developed by unsen and Kirchoff about 1859 to 1860 and were immediately ilized by them in a search for new elements. In this they ere successful for in 1860 they announced the discovery of a w alkali metal whose spectrum was characterized by two ight blue lines and hence was named Cesium, Cs, from cæsius, e Latin word for the blue of the clear sky. Again, in 1861, they scovered another alkali metal whose spectrum consisted of two ry strong lines in the violet and a number of others in the red, llow and green portion of the spectrum. Two of the red lines e deeper red than the potassium lines, and hence the element s called Rubidium, Rb, from rubidius the Latin word for the rkest red color.

Rubidium and cesium are always found in connection with hium, sodium, and potassium. They are so like one another d so very much like potassium that it is a difficult matter to parate them not only from each other but also from potassium.

Metallic rubidium and cesium may be obtained by heating eir corresponding hydroxide with powdered magnesium.

Rubidium is a brilliant silver white metal which melts at 38.5° d boils at 696°. It has a density of 1.52 and acts upon water en more vigorously than potassium. The hydroxide so formed, OH, is at least as strong as that of potassium. The atomic ight of rubidium is 85.45.

Metallic cesium has a silver white color, melts at 26.5° and ils at 670°. Its density is 2.4. It is even more active chemicy than rubidium. Cesium hydroxide, CsOH, is a very strong se, and its salts are isomorphous with those of potassium and bidium. The atomic f cesium is 132.81.

Potassium, rubidium and cesium form a triplet of very clos related elements. The difference between the atomic wei of potassium, 39.1 and that of rubidium 85.45 is 46.35 whic just about that between rubidium and cesium which is 47. The same sort of relation exists between the triplet formed chlorine, bromine, and iodine and here, too, the difference atomic weight is about the same, being roughly 45. In a g many ways the properties of these three elements vary i regular manner with the atomic weight as may be seen from following table.

As the atomic weight of the metal increases.
The chemical activity of the metal increases.
The solubility of the hydrotartrate increases.
The solubility of the sulfate increases.
The solubility of the chloride increases.
The solubility of the chlorplatinate decreases.
The solubility of the alum decreases.
The boiling and melting points of the metals decrease.

AMMONIUM

In the discussion of ammonia, NH_3, it was pointed out this substance would combine directly with acids for ammonium salts. For example, ammonium chloride, N is formed by the union of ammonia and hydrogen chl

$$NH_3 + HCl = NH_4Cl$$

Ammonium chloride when dissolved acts as though it dissociated into chlorine as ion and the complex cation N called the ammonium ion. This ion forms a long list of salt is so very similar to potassium in its properties that it wou entirely out of place not to discuss it here in connection wit element. Most of the ammonium salts are isomorphous the corresponding compounds of potassium, and the ammo ion gives difficultly soluble compounds with the same rea that the potassium ion does. So it is a rather easy mat mistake the ammonium ion for the potassium.

The sources and methods of preparation of some of th monium compounds have already been mentioned in co with the discussion of the compounds of nitrogen, pp. –194.

mmonium Hydroxide.—Ammonium hydroxide is formed n ammonia dissolves in water, and may be obtained at low peratures as a solid which melts at −79°. Its solution ws comparatively weak basic properties indicating a small centration of hydroxyl.

mmonium Chloride.—Ammonium chloride or sal ammoniac, I_4Cl, is one of the more important of the ammonium salts. s easily soluble in water, and crystallizes in cubes or octahedra. solutions are slightly acid due to hydrolysis. When heated about 350°, it decomposes into ammonia and hydrogen chloride ich pass off as gases, and recombine when they reach a cooler ce, forming ammonium chloride, hence ammonium chloride volatile. Most other ammonium salts undergo similar decomsition when heated giving ammonia and the acid. It is used making dry cells and some other kinds of electrical batteries, a reagent in the laboratory, in soldering and in medicine. me idea of the extent of the use of ammonium chloride in teries may be gathered from the fact that 50,000,000 dry cells made in this country every year.

mmonium Nitrate.—Ammonium nitrate, NH_4NO_3, is a white stalline salt. At temperatures somewhat higher than its lting-point, 160°, ammonium nitrate decomposes into nitrous de and water;

$$NH_4NO_3 = N_2O + 2H_2O$$

n this respect, it differs from most of the other ammonium s since it does not yield ammonia and the acid. The differe is presumably due to the oxidizing action of the nitric acid ammonia. The nitrous oxide is a powerful oxidizing agent; this reason the nitrate is used in some explosives, in fact under eptional conditions it is explosive without any admixture.

mmonium Sulfate.—Ammonium sulfate, $(NH_4)_2SO_4$, is in ne ways the most important of the ammonium salts. It is ained in the recovery of ammonia in the gas works, and is the ting-point for the preparation of most of the ammonium npounds. It is ex y used for this purpose, b as a nitrogen fertilizer, something like 500,000 tons of it being used for agricultural purposes each year.

It is a white crystalline salt isomorphous with potassium sulfate.

The Sulfides of Ammonia.—Ammonium hydrosulfide, NH_4HS, is formed when equal volumes of ammonia and hydrogen sulfide are brought together. It is lline substance which readily decomposes into its constitue

The salt is easily soluble in er and gives the ammonium and hydrosulfide ions.

Two volumes of ammonia and e of hydrogen sulfide unite to form ammonium sulfide, (NH This is much less stable than the acid salt and passes qui o the latter with the loss of ammonia. When dissolved ter, it is largely hydrolyzed giving ammonium hydroxide a he hydrosulfide ion, HS^-.

Solutions of these salts may be made by passing hydrogen sulfide into ammonium hydroxide solution. They are used as reagents to furnish the sulfide ion S^{--} and hydrosulfide HS^- which are necessary for the precipitation of such sulfides as required a higher concentration of sulfur as ion than is furnished by hydrogen sulfide, the sulfides of manganese and zinc for example.

A solution of ammonium sulfide will dissolve sulfur, and thereby acquires a yellow color and is then known as yellow ammonium sulfide. It contains polysulfides and is used as a reagent.

Ammonium Carbonate.—When an excess of carbon dioxide is passed into a solution of ammonium hydroxide, ammonium bicarbonate, NH_4HCO_3, is formed.

$$NH_4OH + CO_2 = NH_4HCO_3$$

This is a fairly stable white crystalline salt which is soluble in water. The solid has a slight odor of ammonia and tends to decompose into ammonia, water and carbon dioxide. This reaction is quite rapid at moderately elevated temperatures and is employed by bakers who use the bicarbonate as a leavening agent much as the housewife does baking powder. For this purpose, the bicarbonate has the distinct advantage over the aking powder that it leaves practically no foreign substance in e food.

An excess of ammonium hydroxide will convert the bicarbonate to the carbonate, $(NH_4)_2CO_3$, but this is very unstable and soon ecomposes.

Commercial ammonium carbonate is made by subliming a ixture of the sulfate and powdered calcium carbonate. It is a ixture of the bicarbonate and carbamate, $NH_4CO_2NH_2$. The tter is formed when ammonia combines with carbon dioxide.

Ammonium Oxalate.—Ammonium oxalate, $(NH_4)_2C_2O_4 \cdot 2H_2O$ made by neutralizing oxalic acid with ammonium hydroxide. is a white crystalline salt soluble in water and much used as a agent.

Ammonium Thiocyanate.—Ammonium thiocyanate, NH_4NCS, very easily soluble in water and is exceedingly poisonous. is much used as a reagent.

Analytical Reactions of Ammonium.—The ammonium ion rms difficultly soluble compounds with the cobaltinitrite, chlorolatinate, and hydrotartrate ions. These compounds cannot be istinguished by the eye from the corresponding potassium mpounds. Ammonium compounds, however, do not give a ame test or spectrum when introduced in the Bunsen flame.

A very sensitive and characteristic test for ammonium comounds is based upon the fact that when a soluble base like dium hydroxide is added to an ammonium salt, undissociated nmonium hydroxide is formed owing to the weakly basic aracter of this substance. As soon as the ammonium hydroxe is formed it breaks down into water and ammonia. The tter may be easily detected by its odor or by its action on oistened red litmus which is turned blue when held in the pors over the solution. The equations for reactions in the lution are as follows.

$$NH_4^+ + Cl^- + Na^+ + OH^- \rightleftarrows NH_4OH + Na^+ + Cl^-,$$
$$NH_4OH \rightleftarrows NH_3 + H_2O$$

e ammonia then vaporizes and dissolves in the water on the mus where the following reactions take place

$$NH_3 + H_2O \rightleftarrows NH_4OH \rightleftarrows NH_4^+ + OH^-$$

d it is this hydroxyl which turns the litmus blue.

Of course potassium compounds can do nothing like this so it is very easy in this way to distinguish between the two sets of compounds.

Ammonium Amalgam.—The great similarity between the ammonium ion and the potassium ion suggests that if free ammonium, NH_4, could be obtained it would be metallic in character. Attempts to prepare free ammonium have so far been unsuccessful, but an amalgam of this su[illegible]ce and mercury can be made either by electrolyzing most am[illegible]nium salts (the nitrate will not do), using a mercury cath[illegible]or by the action of sodium amalgam on an ammonium sa[illegible]tion.

Below −85° the amalgam is [illegible]ard stable substance, but at ordinary temperatures it is very sp[illegible]ngy and consists largely of a mass of bubbles due to the deco[illegible]osition of the dissolved ammonium into hydrogen and am[illegible]nia. That ammonium has metallic characteristics is shown by the fact that it dissolves in mercury which will not dissolve anything else that is not a metal.

LITHIUM

The element lithium is very widely distributed and is obtained from petalite, $LiAl(Si_2O_5)_2$, and lepidolite or lithium mica. The metal is prepared by the electrolysis of the fused chloride. It is a solid with a silver white luster, melts at 186° and boils above 1400°. Its density is 0.594 so that it floats on the petroleum used for its preservation.

The atomic weight of lithium is 6.94 making it the third element in the order of atomic weights. It is active chemically but less so than the other members of the alkali group. It reacts rapidly with water but the metal does not melt and the hydrogen is not inflamed. It burns when heated in air, hydrogen, chlorine, bromine, iodine, sulfur, or nitrogen. This last property is interesting and somewhat important because there are not many things which will combine so readily with nitrogen. Lithium nitride, Li_3N, is formed.

Perhaps the most significant properties of lithium are that its phosphate, Li_3PO_4, and its carbonate, Li_2CO_3, are rather difficultly soluble in water, and that the bicarbonate $LiHCO_3$ is more soluble than the carbonate. With every other alkali metal, the bicarbonate is less soluble than the carbonate and the phosphate is easily soluble. The phosphates and carbonates of the members of the next group in the periodic system are difficultly soluble and the bicarbonates are more soluble than the corresponding carbonates. This shows that lithium has properties that make it a sort of connecting link or transition element between the two groups. That it really belongs to the alkali metals and not with the Group II is shown by the fact that it is monovalent while the members of Group II are divalent.

Beryllium, the first member of Group II, is like lithium in that it has properties which connect it with both Groups II and III.

In many ways it would have been more logical to have opened the discussion of the metals with that of lithium, but its postponement until this point just before taking up Group II is justified by the properties mentioned above.

Lithium Carbonate.—Lithium carbonate Li_2CO_3 is commercially the most important lithium salt. It is used in medicine and for the preparation of lithium salts.

Lithium Chloride.—Lithium chloride is used in making artificial mineral waters and for making red fire and other fireworks.

Analytical Properties of Lithium.—Lithium is very easily detected by the fact that it imparts a bright red color to the Bunsen flame and that its spectrum contains a very strong red line which is visible even when the lithium is present in exceedingly small quantities.

CHAPTER XXII

[illegible] I

Ra←Ba←Sr [illegible] Mg→Zn→Cd→Hg
Alkaline earth [illegible] agnesium sub-group

General.—The first n [illegible] oup II in the periodic system is beryllium. As menti [illegible] thium, beryllium has properties which connect it bo [illegible] p II and with Group III and therefore its discussion [illegible] ned until a later point. The other members of the grou [illegible] urally into two well-marked sub-groups; the one called the alkaline earth metals and comprising the common metals, calcium, strontium, and barium, and the very rare element radium; and the other sub-group called the magnesium family containing beryllium, magnesium, zinc, cadmium, and mercury. All the members of the group are divalent, but mercury also forms a series of compounds in which it is monovalent.

Calcium, strontium, and barium form a triplet of very closely related elements, and for a long time have been grouped together under the name of the alkaline earth metals. The discussion of the group will be opened with that of these metals since they are in many ways more closely connected with the alkali metals than are the members of the magnesium sub-group.

THE ALKALINE EARTH METALS

CALCIUM

The compounds of calcium have been known and used from the very earliest times, but the element itself was first prepared, although in an impure state, by Davy in 1808.

Occurrence.—Calcium compounds are very abundant and are widely distributed over the earth's surface in the form of silicates, carbonates (limestone), sulfates, fluoride, phosphates, borates,

. The element is present in the sun and certain of the fixed rs as shown by their spectra.

Compounds of calcium are indispensable for the growth and of plants and animals. The bones and teeth of animals are nposed largely of calcium phosphate but contain some carıate and fluoride in addition.

Preparation of the Element.—Calcium is prepared on a ·ly large scale by the electrolysis of the fused chloride, the)de consisting of carbon and the cathode of an iron rod. e calcium, as it is liberated, clings to the end of the rod and latter is gradually withdrawn from the fused salt, causing calcium to build up an irregular cylinder of the metal. It is ential that the temperature of the fused calcium chloride be)t as low as possible; for this purpose, calcium fluoride is netimes added to the bath, since it dissolves and lowers the lting-point of the chloride.

Properties.—Calcium is a silver white crystalline metal which lts at 800° and volatilizes below its melting-point in a vacuum. has a density of 1.55 and is malleable, although somewhat ·der than lead. It tarnishes rapidly in moist air at ordinary nperatures, but may be turned and polished in the air if kept ;.

Calcium decomposes water, forming hydrogen and calcium lroxide, $Ca(OH)_2$. It acts vigorously on acids. When heated the air, it burns brilliantly and also combines rapidly at higher nperatures with nitrogen, chlorine, hydrogen, sulfur, silicon, l phosphorus. With nitrogen, calcium nitride, Ca_3N_2, is med. When calcium is heated in a closed vessel, both the 'gen and nitrogen are removed and a very high vacuum ults.

The atomic weight of calcium is 40.07.

Calcium Hydride.—Calcium combines directly with hydrogen form calcium hydride, CaH_2, a white crystalline substance ich reacts with water, forming the hydroxide and hydrogen.

Calcium Oxide.—Calcium oxide, or lime, is a very important stance as everyone knows. It does not occur in nature, but eadily prepared by heating marble or limestone to a high ıperature when the following reaction takes place,

$$CaCO_3 \rightleftarrows CaO + CO_2$$

This reaction is reversible and the conditions governing it will be considered in detail under calcium carbonate.

This process is carried out in furnaces called lime kilns. The more modern types of these kilns, Fig. 56, consist of a tall shaft of brick work with the interior somewhat egg-shaped in cross section, with two or more fire boxes l the sides and opening into t a short distance from the bo The flame and hot gases fr uel are drawn into the shaft anc the limestone above its tem re of decomposition, while the awn in by the draft of the s ps away the carbon dioxide a vers the temperature necessary for the decomposition. The operation is continuous, the limestone being fed in at the top as fast as the lime is removed at the bottom. This country produces nearly four million tons of lime per year.

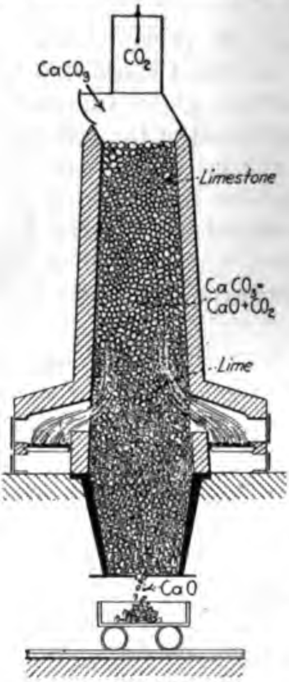

FIG. 56.

Calcium oxide is a white substance having a density of 3.3. It shows some signs of melting when heated in the oxyhydrogen blowpipe and under such conditions gives a very bright light which is known as the calcium or lime light.

The melting-point of lime is about 1900° and it not only melts easily at the temperature of the electric furnace, but even boils. When the vapors of the oxide condense, crystals of calcium oxide are formed. Calcium oxide is not reduced by sodium or by carbon except at temperatures of the electric furnace. The calcium obtained by the reduction with carbon unites with more carbon to form the carbide, CaC_2.

Lime has a great tendency to combine with water forming the hydroxide, $Ca(OH)_2$. Because of this, it is used in drying ammonia and certain other gases and in dehydrating alcohol. Its st important use, however, is in the preparation of mortar and ment.

Calcium Hydroxide.—Calcium hydroxide or slaked lime, $(OH)_2$, is made by the action of water on calcium oxide or icklime as it is sometimes called. The equation is,

$$CaO + H_2O = Ca(OH)_2$$

The action is slow in starting but evolves considerable heat, that after the reaction has once begun the temperature rises nd it then goes on rapidly. When large quantities of lime ake in contact with wood, the temperature often rises igh enough to set fire to the wood. In this way buildings ntaining lime in storage are sometimes set on fire by water times of floods.

Calcium hydroxide is a white powder whose density is 2.08 d which therefore occupies a larger volume than the lime from hich it was formed. It is slightly soluble in water, 600 parts the latter being required for one of the hydroxide at ordinary mperatures, and about twice as much water at the boiling-int since the solubility of the hydroxide decreases with rising mperature. The solution is decidedly alkaline in character cause calcium hydroxide is a strong base, although not as strong sodium hydroxide. The solution of the hydroxide is called me water and is used in medicine and as a reagent for the etection of carbon dioxide.

Because of its cheapness, calcium hydroxide is largely used herever a base is desired, unless the properties of the calcium n interfere. If the presence of much water is objectionable, a uspension of the hydroxide in water called milk of lime is used. hat part which is actually in solution reacts first and then more issolves so that ultimately it may all be used.

Slaked lime is used in the manufacture of sodium and potas-ium hydroxides, ammonia, bleaching powder, mortar, the oftening of water, the purification of illuminating gas, the emoval of hair from hides, and for many other purposes.

Air-slaked lime is lime which has been exposed to the air ntil it has fallen to powder from the water and carbon dioxide aken up from the air; it contains calcium oxide, hydroxide, nd carbonate.

fore c_3 the concentration of the CO_2 is constant for equilibrium at any one temperature. The concentration of a gaseous substance is proportional to its pressure, so it follows that the carbon dioxide in equilibrium with the CaO and $CaCO_3$ at any given temperature will always have a certain fixed pressure.

The decomposition of the calcium carbonate is accompanied by the absorption of heat, an refore in accordance with the law of mobile equilibrium essure of the carbon dioxide increases with rising temper It reaches atmospheric pressure at about 900°, but in a of air or any other gas which will keep the partial pres carbon dioxide low by sweeping it away as fast as it is , the decomposition will take place at a much lower te e. In the lime kiln the limestone is heated in a curren s in which the partial pressure of carbon dioxide is far low n one atmosphere, and consequently the temperature of decomposition is comparatively low.

Calcium carbonate although so slightly soluble in water readily dissolves in acids. This of course is another case of a difficultly soluble salt of a weak acid being dissolved by a stronger acid.

Calcium Chloride.—Calcium chloride, $CaCl_2$, occurs in nature in sea water and as a constituent of a few minerals for example, tachhydrite, $CaCl_2 \cdot MgCl_2 \cdot 12H_2O$, and apatite, $Ca_5(PO_4)_3Cl$.

It may be prepared by dissolving pure calcium carbonate in hydrochloric acid. It is a by-product of several technical processes and is comparatively cheap. It is exceedingly soluble in water and crystallizes with varying amounts of water of crystallization forming a mono, di, two tetrahydrates and hexahydrate. The hexahydrate crystallizes from highly concentrated solutions at ordinary temperatures. It is very deliquescent and melts at 30°. When mixed with ice in the best proportions, a temperature of −55° may be obtained. Anhydrous $CaCl_2$ and ice do not make a good freezing mixture since the salt evolves much heat in dissolving, while the hexahydrates absorb heat.

When the hexahydrate is heated to 200°, it loses four mol water and forms a white porous mass of the dihydrate whi very hygroscopic and is used for drying gases. Wh to a still higher temperature the anhydrous salt is e reaction represented by the following equation takes place to certain extent,

$$CaCl_2 + H_2O = CaO + 2HCl$$

d the product contains some calcium oxide.

Calcium chloride forms a compound, $CaCl_2{\cdot}8NH_3$, with monia and cannot be used for drying this substance.

Calcium Hypochlorite and Bleaching Powder.—Bleaching wder, $CaCl_2O$, or chloride of lime, is made by the reaction of orine on slacked lime,

$$Ca(OH)_2 + Cl_2 = CaCl_2O + H_2O$$

In the most recent plants, the slacked lime is carried in a nveyer in a direction contrary to that of the chlorine so that e almost saturated lime meets the strongest chlorine, while e fresh lime comes in contact with the weakest chlorine. In s way, each is utilized to the greatest advantage. (For the operties and use of bleaching powder see pp. 128, 133.)

Pure calcium hypochlorite, $Ca(OCl)_2$, may be prepared by utralizing hypochlorous acid with calcium hydroxide. It ds no application.

Calcium Bromide and Iodide.—Calcium bromide and iodide are ry similar to the chloride, but are even more soluble than the ter.

Calcium Fluoride.—Calcium fluoride, CaF_2, or fluorspar as it commonly called, occurs in nature fairly abundantly. It stallizes in cubes and is nearly insoluble in water. It melts 1,330° and has to a marked degree the property of reducing melting-point of the slags produced in metallurgical processes d has long been used for this purpose. When heated it benes luminous at temperatures far below redness, and this es rise to the term fluorescence.

Calcium fluoride is the source of other fluorine compounds, d is used in the preparation of hydrofluoric acid for etching ss and for other purposes.

alcium Nitrate.—Calcium nitrate, $Ca(NO_3)_2$, is found in all ile soils. It may be made by the action of nitric acid on carbonate, and is manufactured on a large scale for use as rtilizer at the plant for the manufacture of nitrogen compounds from the air at Notodden, Norway. It is very soluble in water and forms a number of hydrates; that stable at ordinary temperatures is $Ca(NO_3)_2 \cdot 4H_2O$. The anhydrous salt is used as a drying agent. When heated it gives calcium oxide, nitrogen peroxide, and oxygen.

Calcium Sulfate.—Calcium sulfate, $CaSO_4$, occurs in nature in two forms as anhydrite, [illegible] d as gypsum, $CaSO_4 \cdot 2H_2O$; the latter is the more import[illegible] from it is made the valuable plaster of Paris and cement pl[illegible]

Calcium and sulfate ions [illegible] nt in sea water and gypsum is deposited soon after the c[illegible] ation of such water begins. Without doubt this has b[illegible] origin of the great beds of gypsum which are found in [illegible] s parts of the world. The United States has many [illegible] sits, notably in New York, Michigan, Iowa, Ohio, [illegible] ahoma, and Kansas. The total production of gypsum in the United States is about 2,500,000 tons per year, of which two-thirds is converted into plaster.

Besides the dihydrate or gypsum, $CaSO_4 \cdot 2H_2O$, calcium sulfate forms a hemihydrate, $2CaSO_4 \cdot H_2O$, which is in equilibrium with the dihydrate and water vapor at 107° under a pressure of one atmosphere. When ground gypsum is heated from 110 to 130° its aqueous tension is greater than one atmosphere, and it rapidly decomposes, losing water and changing into the hemihydrate. The product obtained in this way is called plaster of Paris. When mixed with water to form a paste, it quickly hardens to a mass of interlaced crystals of the dihydrate. In so doing it increases materially in volume and fills perfectly a mould into which it may be poured; because of this it is much used in making plaster casts. By far the more extensive use for this product is as a plaster for the interior of buildings, and for such purposes the plaster of Paris sets too quickly. To overcome this, advantage is taken of the fact that many organic substances such as glue, sugar, glycerine, etc., will greatly increase the time of setting; such substances are called retarders and the plaster so treated is known as cement plaster. Cement plaster may also be made without retarder by using gypsum which is mixed with the proper amount of clay or dirt.

These plasters have many advantages over lime plasters for inside work and have very largely replaced them. One important advantage is that they dry quicker and are much harder and stronger than the lime plasters. If plaster of Paris is mixed with a solution of common salt instead of pure water, its time of setting will be shortened.

Great care must be taken not to overheat the plaster or drive off all the water, since in these cases the plaster either will be too slow in setting or will not set at all. Such plaster is said to be "dead burned."

The solubility of gypsum varies in a rather remarkable way with the temperature; from 0° to 38°, the solubility increases and then decreases as the temperature rises. At the boiling-point of water, in a steam boiler working under the usual pressure, calcium sulfate is nearly insoluble; and under such conditions, it is precipitated from water which contains much of this substance, in the form of a scale which clings closely to the boiler. Hard boiler scale often consists largely of calcium sulfate. Waters containing this substance are said to have permanent hardness in distinction from temporary hardness due to the bicarbonate. The addition of the proper amount of sodium carbonate will precipitate the calcium as carbonate and leave a solution of sodium sulfate. In this way the permanent hardness may be removed.

Calcium Sulfide.—Calcium sulfide, CaS, is made by heating the sulfate with charcoal. It is a by-product of the Le Blanc soda process, and is insoluble in water; but is slowly hydrolyzed forming calcium hydroxide and the hydrosulfide,

$$2CaS + 2H_2O = Ca(OH)_2 + Ca(HS)_2$$

Many specimens of calcium sulfide especially if slightly impure with compounds of vanadium and bismuth will phosphoresce, *i.e.*, shine in the dark, after being exposed to the light. The pure sulfide does not do this.

Calcium Phosphate.—The principal forms in which calcium phosphate occur in nature are apatite, $Ca_5(PO_4)_3F$ and the normal phosphate, $Ca_3(PO_4)_2$. Its chief commercial source is from phospherite whose composition lies between that of apatite and the normal salt. Enormous beds of phosphate are found in many parts of the world; notably in this country in Florida, Tennessee, South Carolina, Utah and its neighboring States. The western deposit is the largest in the world and will doubtless at a future time furnish a large part of the supply.

Calcium phosphate is present in nearly all rocks and all fertile soils. It is practically insoluble in pure water, but is very slowly dissolved by the carbonic acid which is present in the ground waters. Compounds of [illegible]s are absolutely essential to all forms of life. Animals [illegible] what they need principally from plants, while the la[illegible] theirs from the phosphate rendered soluble by the ca[illegible]d.

Although most soils con[illegible]e aggregate large quantities of calcium phosphate, th[illegible]f the weather in rendering this soluble is too slow t[illegible] demands of the crops under intensive cultivation an[illegible]lants must be fed with ready prepared soluble phospha[illegible] this purpose many millions of tons of phosphorite are mined each year and made into "superphosphate" fertilizer.

The phosphate fertilizers are made by mixing approximately equal quantities of phosphorite and chamber-sulfuric acid. The dihydrates of calcium sulfate and monocalcium phosphate are formed as shown in the following equation:

$$Ca_3(PO_4)_2 + 2H_2SO_4 + 6H_2O = Ca(H_2PO_4)_2{\cdot}2H_2O + 2CaSO_4{\cdot}2H_2O$$

This reaction takes place with the evolution of heat, and the mixture soon solidifies to a mass composed of the two hydrated salts. This is known as superphosphate. The monocalcium phosphate is easily soluble in water, and is the more valuable part of the fertilizer.

Besides the tricalcium phosphate or normal phosphate as it is called, $Ca_3(PO_4)_2$, there is known the dicalcium salt, $CaHPO_4$, and the monosalt given above. All the calcium phosphates are readily soluble in acids, even in those as weak as acetic acid. This is due to the fact that phosphoric acid is weak and that ion, $H_2PO_4^-$, is formed with especial ease. The calcium salt of t ion is easily soluble as has been mentioned above.

Besides being made into fertilizers, calcium phosphate as the source of phosphoric acid and phosphorus.

alcium Carbide and Calcium Cyanamide.—Calcium carbide, $_2$, is formed by the reaction of carbon upon lime in an tric furnace (Fig. 57). The equation for the reaction is,

$$CaO + 3C = CaC_2 + CO$$

carbide reacts with water producing acetylene, and with ogen for the formation of calcium cyanamide, $CaCN_2$,

$$CaC_2 + N_2 = CaCN_2 + C$$

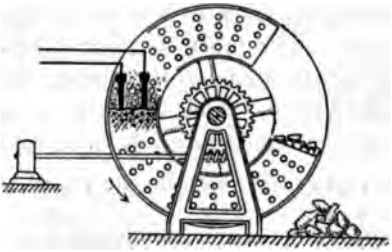

Fig. 57.

s reaction takes place at 1,000° and goes more readily in the sence of calcium chloride. Calcium cyanamide is slowly omposed by water, forming the carbonate and ammonia,

$$CaCN_2 + 3H_2O = CaCO_3 + 2NH_3$$

is therefore useful as a nitrogen fertilizer, and is now being de at Niagara Falls in the United States, and in about fourteen erent places in the world. While the nitrogen fertilizers are y important, they are not as absolutely indispensable as the sphates and potassium fertilizers are since it is practicable ntroduce the nitrogen compounds into the soil with leguminous nts.

alcium Oxalate.—Calcium oxalate, CaC_2O_4, is a white crystal- salt which is very slightly soluble in water and is formed at e whenever a solution of an oxalate is added to a calcium . The precipitate is practically insoluble in water and in tic acid, but dissolves easily in strong acids like hydrochloric nitric. The explanation for the difference is to be found in fact that oxalic acid is a stronger acid than acetic, but ker than hydrochloric. It will be recalled that the difficultly soluble salts of weak acids are soluble in the stronger acids because of the decrease in the concentration of their anion due to the formation of the undissociated weak acid. The slight solubility of calcium oxalate is made use of in the detection and estimation of calcium as ion. The oxalate reagent used is ammonium oxalate.

Calcium Silicate and Glass.—Calcium silicate occurs in nature in almost all of the r [illegible] s. The meta silicate, $CaSiO_3$, forms the mineral w [illegible] is not of much importance.

The artificial comp [illegible] known as glass are, however, of great importance. [illegible] ommon of these, that known as soft or soda glass, is ma [illegible] m calcium carbonate, sodium carbonate, and glass san [illegible] is nearly pure silicon dioxide. The reaction may be [illegible] d by the following equation:

$$Na_2CO_3 + CaCO_3 \ [illegible] = Na_2CaSi_6O_{14} + 2CO_2$$

but it must be understood that the glass is a mixture of silicates rather than a definite chemical compound.

The substances are mixed in the proper proportions and heate to a temperature below their melting point when the reactio takes place, and most of the carbon dioxide escapes through th porous mass. The temperautre is then raised to about 1,20 when the glass fuses to a mobile liquid which is fluid enough t allow the bubbles of gas to escape. The temperature is the lowered to 700° or 800° when the glass becomes viscous enough work. Ordinary window glass is made by blowing long cylindric bulbs of glass. After the bulb is blown to the proper dimensio the bottom is heated and blown out leaving a long cylinder wi a bottle-like top and neck. This is allowed to cool and the t cut off by wrapping a string of hot glass around the cylinder ne the top and suddenly touching a heated spot on the cylinder wi a cold iron. A crack instantly extends around the cylind following the line heated by the string of hot glass. The res is a long glass cylinder open at each end. This is then sp lengthwise by running a red hot iron through the cylinder a touching the heated glass at the end with a cold iron. T crack instantly runs the whole length of the cylinder. This then placed upon a flat revolving bed of a furnace upon whi it is smoothed out after being heated to the softening poi

Bottles are blown into moulds, but flasks, beakers, etc., are made free hand without any moulds, the glass blower taking advantage of the fact that the surface tension of the glass will cause it to contract when heated, while he can make it expand at will by blowing into the vessel when it is hot. Glass tubing is made by rapidly drawing out a hollow mass of glass. This is done by two men who walk or run in opposite directions. Pressed glass articles are made by pressing the hot glass in moulds having the desired designs cut upon them. The designs in cut glass are worked into the glass with rapidly revolving wheels, armed with wet sand which quickly cuts away the glass. The surface is afterward polished. Plate glass is made by casting the glass into large sheets which are ground until the sides are plane and parallel, and then polished.

The cheaper kinds of soda glass are often made from sodium sulfate, carbon, calcium carbonate, and sand, the equation being,

$$2Na_2SO_4 + C + 2CaCO_3 + 12SiO_2 = 2Na_2CaSi_6O_{14} + 3CO_2 + 2SO_2$$

Soda glasses are rather easily attacked by water, and for many chemical purposes the more difficultly soluble and less fusible potassium glass is made; this is practically the same as the soda glass except the potassium has taken the place of the sodium. Its composition may be represented by $K_2CaSi_6O_{14}$. It is commonly called hard or Bohemian glass. Curiously enough a glass composed of a mixture of soda and potash glass is more soluble than one containing either alone.

Many special glasses are made in which the sodium, potassium, and calcium are replaced more or less completely by lead, magnesium, zinc, barium, antimony, arsenic, aluminum, lithium, didymium, thallium, iron, manganese; and the silica by boric or phosphoric oxides. Flint glass, crystal glass, and Strass are potassium lead glasses and have great brilliancy and a high index of refraction. They are easily attacked by water and acids, and are not suitable for chemical purposes, but are used in optical instruments. One kind of Jena glass is especially resistive to chemical action and is a borosilicate glass containing zinc and barium.

Molten glass will dissolve ny metallic oxides whi impart characteristic colors. Cobalt gives blue, chromium and copper oxides green, uranium yellow with a greenish fluorescence, cuprous oxide with a reducing agent, selenium and metallic gold a deep red color due to a colloidal solution of the elements. Milk glass is made by adding bone ash (calcium phosphate) or stannic oxide, SnO_2, to the glass. These do not dissolve, but make the glass white and opaque.

Glass is an amorphous sub[illegible] and has no definite melting point; it simply graduallv s[illegible]s the temperature is raised. This has led many to con[illegible]t ordinary temperatures as a very viscous liquid, but it ce[illegible]s highly elastic and has the general properties of a solid. [illegible] glass is kept for a long time at temperatures near its soft[illegible]point, it gradually becomes crystalline or devitrifies as it [illegible]ed. With certain kinds of glass, this seriously interferes [illegible]s working.

All thick glass objects, especially if of irregular shape, must be cooled very slowly, annealed as it is called. If cooled quickly, the outside will harden while the inside is still soft; upon further cooling, the interior tends to contract and this puts great stress upon the glass and makes it extremely likely to crack. A piece in this condition will often fly into minute fragments when scratched at any point on the surface.

Analytical Properties of Calcium.—The more important analytical properties of calcium have been given in connection with the oxalate. In addition it may be mentioned that volatile calcium compounds, the chloride for example, color the Bunsen flame brick red and give a red and a green band in the spectroscope (see Frontispiece). The latter test is quite sensitive.

STRONTIUM

Strontium is the second member of the alkaline earth metals, if they are arranged in the order of their atomic weights.

Both the physical and chemical properties of the element and of its compounds closely resemble those of calcium an
calcium salts. It is, however, much less abundant
tively unimportant.

The metal may be prepared by electrolv
chloride; it is silvery white and crystalline.

nd volatilizes at 950° in a vacuum. The density is 2.5. It is ore rapidly oxidized in air than calcium and decomposes ater and alcohol. It dissolves very rapidly in acids. When eated in oxygen it burns with a bright red flame. It combines ith most of the non-metallic elements. The atomic weight strontium is 87.63.

Occurrence.—Strontium occurs in nature as strontianite, the rbonate, $SrCO_3$, isomorphous with aragonite and as celestite. SO_4, isomorphous with anhydrite, $CaSO_4$.

The Compounds of Strontium.—Besides the naturally occurng carbonate and sulfate, the principal compounds of strontium e the chloride, $SrCl_2{\cdot}6H_2O$, the nitrate $Sr(NO_3)_2$, the oxide, O, the hydroxide $Sr(OH)_2$, and the oxalate SrC_2O_4. The lts may be easily made from the carbonate by treating the tter with the acid corresponding to the salt desired. The xide may be made by a similar method to that used for calcium xide, that is by heating the carbonate; but the temperature equired is far higher than that for calcium oxide, so a better ay is to heat strontium nitrate. The hydroxide may be easily ade by passing superheated steam over the carbonate,

$$SrCO_3 + H_2O \rightleftarrows Sr(OH)_2 + CO_2$$

he steam sweeps away the CO_2 as it is formed and so favors he transformation of the carbonate. Strontium chloride, ulfate and carbonate are less, while the hydroxide and oxalate re more soluble than the corresponding calcium compounds.

Volatile strontium compounds color the flame carmine red and ve a spectrum which consists of a number of strong red lines nd a weaker but more characteristic blue line. The spectroopic test is very sensitive.

BARIUM

Barium is the third element of the alkaline earth family. The etal is silver white and has a density of 3.78. It melts at about 50° and boils at 1,150°. It oxidizes rapidly, sometimes catching re spontaneously, and decomposes water and alcohol even more igorously than strontium. It combines readily with hydrogen

ium is 137.37.

Occurrence.—Barium occurs in nature principally as barytes or heavy spar which is barium sulfate, $BaSO_4$, and as the carbonate or witherite, $BaCO_3$. From these the other barium compounds are made. They are technically much more important than the corresponding strontium compounds. Barium salts may be obtained by treating witherite with the corresponding acid or by reducing the [illegible] sulfide with carbon at high temperatures, and treati[illegible]le with the acid of the desired salt.

Barium Oxide and H[illegible] Barium oxide, BaO, is made by heating the nitrate to a [illegible]perature. It is impracticable to prepare the oxide by h[illegible]e carbonate alone, since the temperature of decomp[illegible]ery high, but a mixture of carbon and barium carbo[illegible]ts easily at a moderate temperature to form barium ox[illegible] carbon monoxide,

$$BaCO_3 + C = BaO + 2CO$$

The formation of the carbon monoxide aids by reducing the partial pressure of the carbon dioxide. The oxide combines even more readily with water than calcium oxide to form the hydroxide which is often called baryta, $Ba(OH)_2$. Because of this, it is feasible to prepare the hydroxide by heating the carbonate in a stream of superheated steam,

$$BaCO_3 + H_2O = Ba(OH)_2 + CO_2$$

The steam decreases the partial pressure of the carbon dioxide, and the opportunity for the formation of the very stable hydroxide aids in the reaction.

The hydroxide is more soluble in water than either the corresponding strontium or calcium compound and is a somewhat stronger base. It crystallizes from its solutions with 8 molecules of water, $Ba(OH)_2 \cdot 8H_2O$.

Barium Dioxide.—Barium dioxide, BaO_2, is formed when either the oxide or hydroxide is heated in a stream of air. At a higher temperature, or lower pressure of oxygen, it decomposes into oxygen and barium oxide. This was the basis of a process for obtaining oxygen from the air. This process has now been replaced by that founded on the liquefaction of the air.

Barium dioxide is important as the starting point for the eparation of hydrogen dioxide.

Barium Carbonate.—Barium carbonate, $BaCO_3$, as has been ntioned, occurs in nature. It is also formed by bringing gether a solution of a carbonate and a barium salt, or by ing the sulfate with sodium carbonate. It is only slightly uble, but more so than the carbonates of calcium or strontium. solubility in water is increased by the presence of carbon xide, owing to the formation of the bicarbonate.

Barium Sulfate.—Barium sulfate, barytes, $BaSO_4$, is in some spects the most important salt of barium. It is the chief urce of the other compounds, and is itself extensively used as a ite pigment, called "permanent white," which is used in ints. The precipitated barium sulfate is more valuable as a gment than the natural because the particles are smaller and nce it has more "covering" power since it is not so transparent. his precipitated sulfate may be obtained by first dissolving itherite in hydrochloric acid, and then adding sulfuric acid hich will precipitate the barium sulfate and regenerate the drochloric acid which is then ready to treat another lot of itherite. It may also be obtained by reducing the sulfate to lfide, BaS, by carbon at high temperatures, and treating the tract from this, which will contain the hydroxide and the drosulfide, with sulfuric acid. The sulfate has some advanges over white lead as a pigment, in that it is chemically inert d cannot change in color, but it does not "cover" as well e p. 422).

Barium sulfate is one of the least soluble salts; 100 grm. of ter will dissolve 0.00026 grm. of the salt at 25°.

Barium Sulfide.—Barium sulfide, BaS, to which frequent erence has been made, is prepared by the interaction of carbon d the sulfate

$$BaSO_4 + 4C = BaS + 4CO$$

is slowly attacked by water, forming the hydroxide and drosulfide.

Barium sulfide is phosphorescent when it contains certain purities, although the pure compound is not.

Barium Chloride.—Barium chloride, $BaCl_2.2H_2O$, is made by heating a mixture of the sulfate with carbon, and calcium chloride, $CaCl_2$,

$$BaSO_4 + CaCl_2 + 4C = BaCl_2 + CaS + 4CO$$

The furnace product is treated with water to dissolve the barium chloride, which is purified by recrystallization. It is not as soluble as calcium chlori[illegible]ot deliquescent. It is much used as a reagent for the [illegible]n and determination of the sulfate ion. Like all the [illegible]ble barium salts it is highly poisonous.

Barium Chlorate.—Bari[illegible]ate, $Ba(ClO_3)_2$, is made by heating together, in solu[illegible]rium chloride and sodium chlorate

$$BaCl_2 + 2Na\text{[illegible]}(ClO_3)_2 + 2NaCl$$

It is used in making green fire.

Barium Nitrate.—Barium nitrate, $Ba(NO_3)_2$, is made by the action of nitric acid upon the carbonate, sulfide, oxide or hydroxide of barium. It crystallizes as the anhydrous salt and sometimes is used in colored fire. It is used in the preparation of the oxide as noted above.

Barium Chromate.—Barium chromate, $BaCrO_4$, is precipitated by bringing together a barium salt in solution and a soluble chromate or dichromate. It has a yellow color and is one of the few colored barium salts. It is but slightly soluble in water and weak acids, but dissolves in strong acids. The chromates of calcium and strontium are very much more soluble than barium chromate, and advantage is taken of this in the analytical separation of the elements.

Analytical Properties of Barium.—The properties of barium which are used in analysis are the slight solubility of the carbonate, sulfate, and chromate together with the green color which it will impart to the Bunsen flame, and the spectrum which consists of a number of orange and green lines. These are much less intense than the lines of calcium and strontium so that this test is not very sensitive. In the separation of the group the members are precipitated together as the carbonates. The precipitate is then dissolved in acetic acid and potassium dichromate added which precipitates barium chromate. The solution is filtered d a dilute solution, 5 grm. per liter, of potassium sulfate added. nce strontium sulfate is much less soluble than calcium sulfate, e concentration of the sulfate as ion in this dilute solution will recipitate strontium sulfate, but not that of calcium. The solu- on is then filtered and ammonium oxalate added to precipitate e calcium.

RADIUM

The remaining member of the group is the very rare element, adium. This was discovered in 1898 by M. and Mme. Curie. t is widely distributed in nature, but always in very small uantities. All rocks and soils seem to contain a very little. t is most abundant in the minerals which contain uranium nd there seems to be a more or less definite ratio between the dium and the uranium content of the ores.

The compounds of radium very closely resemble those of arium, and the corresponding compounds of the two elements e often isomorphous. Radium chloride, bromide, carbonate, nd sulfate are less soluble than the corresponding barium lts. This decrease in solubility is in accord with its higher tomic weight, 226.0. The volatile compounds color the unsen flame carmine red and give two beautiful bands in the d, a line in the blue-green and two weak lines in the violet ortion of the spectrum. The spectrum of radium is so distinct nd characteristic that there can be no doubt but that it is an lement. The radium compounds have the very remarkable roperty of being highly radioactive and of changing sponta- eously into other elements, but the discussion of this phase of e subject will be postponed to a later point when the radio- tive elements may be considered in a group.

Metallic radium has been obtained by first preparing the nalgam through the electrolysis of a solution of radium chloride sing mercury as the cathode, and then carefully driving off the ercury by heating in a vacuum. The radium is left behind as hard silvery white metal. It melts at 700° and is rather more olatile than barium. It blackens in the air, due to the forma- on of a nitride, acts upon water very vigorously. The radio- tivity of the metal is the same as that of an equivalent quantity one of its salts.

General Relationships.—As with the alkali metals, the properties of the alkaline earth elements vary in a regular way with the atomic weight as may be seen from the following table.

As the atomic weight increases.
The reactivity of the element increases.
The density of the element and compounds increases.
The basic properties of e increase.
The solubility of the ases.
The solubility of the unds and nitrate decreases.
The solubility of the omate decreases.

CHAPTER XXIII

THE MAGNESIUM SUB-GROUP

The members of this sub-group, beryllium, magnesium, zinc, dmium, and mercury do not form as well marked a family the members of the alkaline earth metals.

Beryllium is perhaps even more like the next group than it is e the other members of this and so makes a good connecting k between the two groups. Magnesium, zinc, and cadmium ve many points in common but not as many as calcium, rontium and barium. Mercury differs markedly from the hers as will be seen when its compounds are discussed. All e members of the sub-group are more readily reduced to the etallic state than are the members of the alkaline earths and e less active chemically.

BERYLLIUM OR GLUCINUM

The first member of the magnesium group is beryllium or lucinum as it is often called. It got the name glucinum from he fact that its salts have a sweet taste and the name beryllium om its occurrence in the gem stone beryl.

The element does not occur free in nature and its compounds e rare. Neither the element nor its compounds have found any plication except that some of the latter are used as gems. eryl, for example, is a double beryllium aluminum silicate, $e_3Al_2Si_6O_{18}$, which when transparent and green colored is nown as emerald and when having a bluish-green tint as uamarine. The color of emerald is probably due to chromium.

Metallic beryllium may be prepared by the electrolysis of the used double fluorides of sodium or potassium, $BeF_2 \cdot NaF$. is less active chemically than the metals of the alkaline earth roup and decomposes water only very slowly, even when heated. t dissolves readily in the dilute acids, and in solutions of sodium r potassium hydroxides. [illegible] num, the first metallic member of the next group, shows this same peculiarity and this i one of several indications that beryllium gives of its positi the connecting element between Groups II and III. It w recalled that in discussing lithium it was pointed out tha first member of a group often had properties which conn that group with the next higher one.

The chloride, $BeCl_2$, a [illegible] sulfate, $BeSO_4$, are the best k salts. They are both solubl [illegible] water and their solutions acid, owing to hydroly [illegible] he hydroxide, $Be(OH)_2$, is slightly soluble in water [illegible] solves in acids, and also in tions of sodium or pota [illegible] hydroxide.

Beryllium carbonate is [illegible] unstable and decomposes i air at temperatures below [illegible] boiling-point of water int oxide and carbon dioxide.

The atomic weight of beryllium is 9.1.

MAGNESIUM

Magnesium occurs very abundantly in nature as a comp of a large number of silicates of which mention may be m olivine, Mg_2SiO_4, serpentine, $(MgFe)_3Si_2O_7 \cdot 2H_2O$, asb $Ca_3Mg(SiO_3)_4$, meerschaum, $H_2Mg_2(SiO_3)_3 \cdot H_2O$; as the bonate, magnesite, $MgCO_3$, and as a double salt with ca carbonate, $MgCO_3 \cdot CaCO_3$, known as dolomite. The su and chloride and mixtures of the double salts are fou Stassfurt. This by no means exhausts the list of its occu which might be greatly extended.

Preparation of the Metal.—Metallic magnesium is prepared by the electrolysis of fused dehydrated carn $MgCl_2 \cdot KCl \cdot 6H_2O$. The electrolysis is carried out in close tric furnaces through which a current of hydrogen or coal passed to protect the metal from the air.

Magnesium is a silver white metal having a density of It melts at 650° and boils at 1,120°. When heated nearly melting-point it softens and may be pressed into wire whic then be rolled into ribbon. It preserves its luster in d but tarnishes in moist. When heated in the air it burns a very intense light, forming a mixture of the oxide, Mg(the nitride, Mg_3N_2. At a moderately high temperatur tal decomposes steam, forming hydrogen and the oxide. It l burn in carbon dioxide with the deposition of carbon and formation of the oxide. As may be judged from these mples, mangesium is an excellent reducing agent.

The light produced when magnesium burns is especially rich he violet rays which most affect the photographic plates and ice the metal finds application as the active component of ish powder," which may be prepared from powdered magium and potassium chlorate or similar oxidizing agents. th aluminum, it forms useful alloys, which can easily be cast l worked and are lighter than aluminum.

The atomic weight of magnesium is 24.32.

Magnesium Oxide and Hydroxide.—Magnesium oxide, MgO, "calcined magnesia" is prepared by heating the carbonate, ich breaks down into the oxide and carbon dioxide at a much er temperature than calcium carbonate. It is a white, highly isible substance, which is used as a lining for electric furnaces l for crucibles for use in the Goldschmidt process, p. 396. slowly reacts with water to form the hydroxide, $Mg(OH)_2$, ich is only slightly soluble. The solution has a very faint aline reaction, due to the fact that the hydroxide is a weaker e than calcium, as well as being less soluble. Because of its ht solubility the hydroxide is precipitated when a soluble lroxide is added to a magnesium salt. An exception to this ound in the fact that if ammonium salts are present in suffiit concentration, magnesium hydroxide is not precipitated ammonium hydroxide. The explanation is as follows: monium hydroxide is a weak base and the reaction represented the equation,

$$\underset{c_1}{NH_4OH} \rightleftarrows \underset{c_2}{NH_4^+} + \underset{c_3}{OH^-}$$

es place only to a slight extent with the formation of ammon and hydroxyl ions. From the law of mass action, $c_2c_3/c_1 = K$. monium salts are largely dissociated and give a high concenion of the ammonium ion. So, if some ammonium salt, say chloride, be added to an ammonium hydroxide solution, the centration of the ammonium ion, c_2, will be increased and will cause a decrease in the concentration of the hydroxyl ion, c_3, and an increase in that of the undissociated hydroxide c_1. Ammonium hydroxide is then a weaker base in the presence of ammonium salts than when alone; and when the concentration of the salt is high, that of the hydroxyl ion becomes very small indeed.

When ammonium hydroxide is added to a magnesium salt, the reaction is represented by the following equation,

$$\underset{c'_1}{\mathrm{Mg^{++}}} + 2\mathrm{Cl^-} + 2\mathrm{NH_4^+} + \underset{c'_2}{2\mathrm{OH^-}} \rightleftarrows \underset{c'_3}{\mathrm{Mg(OH)_2}} + 2\mathrm{NH_4^+} + 2\mathrm{Cl^-}$$

The conditions for equilibrium are represented by the equation $c'_3/c'_1c'^2_2 = K$. Now, before magnesium hydroxide can be precipitated, the solution must be saturated with the substance; which means the c'_3 must have reached a certain definite value; and hence $c'_1\,c'^2_2$ must have attained a fixed and definite magnitude known as the solubility product or "precipitation value." When ammonium hydroxide is added to a magnesium salt in the *absence* of an ammonium salt, c'_2 is large enough so that $c'_1c'^2_2$ exceeds the solubility product of magnesium hydroxide and this compound is precipitated; but if an ammonium salt is present, c'_2 will be so reduced as shown above that $c'_1c'^2_2$ will be smaller than the solubility product, and $\mathrm{Mg(OH)_2}$ will not be precipitated. Correspondingly, magnesium hydroxide is dissolved by ammonium salts, such as the chloride or nitrate.

This may be shown as follows:

$$\begin{array}{cc|c|l} \mathrm{Mg^{++}} & + & 2\mathrm{OH^-} & \rightleftarrows \mathrm{Mg(OH)_2} \\ c'_1 & & c'_2 & \quad c'_3 \\ 2\mathrm{Cl^-} & + & 2\mathrm{NH_4^+} & \rightleftarrows \mathrm{NH_4Cl} \end{array}$$

$$\frac{c'_3}{c'_1c'^2_2} = K'$$

The ammonium ion from the salt unites with the hydroxyl ions from the magnesium hydroxide, and thereby decreases c'_2; this will, of course, decrease c'_3, and hence increase the solubility of the hydroxide.

Acids would, of course, act in much the same way and decrease the concentration of the hydroxyl ion through the formation of water. Their action, however, is more vigorous than that of ammonium salts. Many other hydroxides are affected in the ne way, so that the general rule may be formulated, that derately soluble hydroxides will be dissolved by ammonium ts and even very difficultly soluble ones by acids, in each ie, because of the decrease in the concentration of the droxyl ion.

Magnesium Carbonate.—The normal carbonate occurs in ture as magnesite, $MgCO_3$. It also combines with calcium bonate to form a compound called dolomite, $MgCO_3$, $CaCO_3$, ich occurs in enormous quantities.

Magnesium carbonate is but slightly soluble in water, although re soluble than the hydroxide. It is more soluble in water ntaining carbon dioxide than in pure water, because of the mation of the bicarbonate.

When a soluble carbonate, such as sodium carbonate, is added a magnesium salt, a mixture of magnesium carbonate and droxide is precipitated. The cause of the precipitation of e hydroxide is found in the fact that the sodium carbonate is drolyzed, giving a certain amount of the hydrocarbonate ion, d of the hydroxyl ion, in addition to the carbonate. Then, ice magnesium hydroxide is even less soluble than the carbone, the two salts are precipitated together.

This mixture prepared by precipitation is washed and dried d put on the market under the name of magnesia alba. It is ed in medicine as a mild alkali.

Magnesium Chloride.—Magnesium chloride, $MgCl_2 \cdot 6H_2O$, is und in the Stassfurt salts and is called bischofite; it is very luble and is highly deliquescent. When it is attempted to hydrate the salt by heating, decomposition takes place and agnesium oxide and hydrochloric acid are formed as shown in e following equation:

$$MgCl_2 + H_2O = MgO + 2HCl$$

Magnesium chloride forms a double salt with potassium loride, $MgCl_2 \cdot KCl \cdot 6H_2O$, which is known as carnallite.

When carnallite is heated it loses its water of crystallization adily but the magnesium chloride is not decomposed. An imonium magnesium double chloride, $MgCl_2 \cdot NH_4Cl \cdot 6H_2O$, morphous with carnallite is known. This may be dehydrated thout decomposition of the magnesium chloride, and when heated to a still higher temperature the ammonium chloride is driven off and anhydrous magnesium chloride is formed.

The term **double salt** has been used a number of times without definition. By it is meant a salt formed by the chemical union of two salts and characterized by the fact that its solution shows the properties of all the ions of the component salts.

A **complex salt** is si[illegible]e salts in that it is formed by the chemical union o[illegible] salts, but differs in that its solutions do not exhi[illegible]rties of the ions of the salts from which it was fo[illegible]ead some of these properties are found to have d[illegible]d to have been replaced by entirely new properti[illegible]

A typical complex s[illegible]m ferrocyanide, $K_4Fe(NC)_6$. This may be formed [illegible] together potassium cyanide, KNC, and ferrous cya[illegible]$_2$,

$$4KNC + Fe(NC)_2 = K_4Fe(NC)_6$$

It might be expected to show the properties of potassium, ferrous, and cyanogen ions, but it shows the properties of potassium as ion and of a new very stable complex ion called ferrocyanogen, $Fe(NC)_6^{----}$, and not the properties of either ferrous or cyanogen ions. A salt of such a complex ion is called a complex salt. Complex salts and double salts gradually merge into one another, so that the difference is one of degree rather than kind.

Magnesium Sulfate.—Magnesium sulfate, $MgSO_4$, occurs in nature as kieserite, $MgSO_4 \cdot H_2O$, epsomite, $MgSO_4 \cdot 7H_2O$, schoenite, $MgSO_4 \cdot K_2SO_4 \cdot 6H_2O$, and in a number of other double salts in the Stassfurt deposits and in other places.

The hepta-hydrate or Epsom salts is an important compound, being used in the manufacture of potassium sulfate from the chloride, as a dressing for cotton goods, and in medicine as a purgative. It is freely soluble in water, and in this way differs strikingly from the sulfates of the alkaline earths and is like the sulfate of beryllium.

Schoenite, $MgSO_4 \cdot K_2SO_4 \cdot 6H_2O$, belongs to a rather of isomorphous salts which have the general forn $m_2AO_4 \cdot 6H_2O$, in which M stands for Mg, Zn, Cd m for K, Rb, Cs, NH_4, and A for S, Se, or Cr racterized by the fact that they readily lose their water of stallization, in general, without the decomposition of the salt other ways.

agnesium Sulfide.—Magnesium sulfide, MgS, is made by direct union of the elements. It is even more readily hydroed than calcium sulfide, owing to the weakness of the hydrox- and its smaller solubility. By boiling the solution, all the fur may be obtained as hydrogen sulfide.

Phosphates of Magnesium.—Magnesium ammonium phosate, $MgNH_4PO_4 \cdot 6H_2O$, is the most important phosphate of gnesium. Because of its slight solubility it is formed whenever gnesium, ammonium, and phosphate ions are brought together. e solution must be alkaline in order to have a sufficient amount the phosphate ion PO_4^{---} present (see sodium phosphate, p. 0), and hence the solution must contain ammonium salts to event the precipitation of $Mg(OH)_2$. The precipitate is of urse soluble in acids, since phosphoric acid is weak. This mpound is analytically the most important of the magnesium lts, since magnesium is always detected and determined rough its formation. When magnesium ammonium phosate is heated, it decomposes into magnesium pyrophosate, $Mg_2P_2O_7$, ammonia and water,

$$2MgNH_4PO_4 = Mg_2P_2O_7 + 2NH_3 + H_2O$$

quantitative analysis, magnesium is weighed as the pyroosphate.

Magnesium Nitride.—Magnesium nitride, Mg_3N_2, is formed the interaction of magnesium and nitrogen at a fairly high nperature. It reacts with water to form ammonia and magsium hydroxide,

$$Mg_3N_2 + 6H_2O = 3Mg(OH)_2 + 2NH_3$$

Analytical Reactions of Magnesium.—Compounds of magsium do not color the Bunsen flame, and consequently no ectrum is to be obtained in this way; but by passing electric arks between pieces of the metal, a characteristic spectrum y be secured. The analytical importance of the magnesium monium phosphate has been discussed. The ion and all of its compounds which do not contain colored anions are colorless.

Water Softening.—Natural waters almost invariably contain bicarbonates, chlorides, sulfates, and occasionally nitrates of calcium, magnesium, sodium, potassium, iron, and aluminum and also some free carbonic acid and silica. Of course, they sometimes contain other salts and acids in addition. For example, free sulfuric acid is often found in mine waters and in river water in the vicinity of factories using this acid.

Waters which contain calcium and magnesium salts are called hard waters and are a source of considerable annoyance and expense in the household, owing to the fact that calcium and magnesium soaps are practically insoluble, and that before a lather can be produced, soap must be added equivalent to all such salts which are present. The calcium and magnesium soaps so produced form a dirty disagreeable scum and are objectionable from every point of view. Many of the calcium and magnesium salts also cause a great deal of trouble and expense through the formation of "scale" in steam boilers, which not only increases the cost of repairs, but also causes a great waste of fuel. Magnesium salts are somewhat hydrolyzed, owing to the weakness of magnesium hydroxide and hence are acid in reaction. This is often the cause of serious pitting of boilers.

It is very desirable, therefore, that the salts of calcium and magnesium be removed from the waters before they are used for domestic or boiler purposes. This may be readily done at a cost far less than that of the soap, repairs and extra fuel, which would otherwise be required. For the removal of the objectionable salts, advantage is taken of the fact that calcium carbonate and magnesium hydroxide are nearly insoluble in water, and the treatment is so managed that these salts shall be precipitated. This is done by adding the proper amount of slaked lime and of crude sodium carbonate, or soda ash as it is called, to the water. The quantities to be added are calculated from the analysis of the mineral content of the water. Before treatment, the average water will contain free carbonic acid, bicarbonates, sulfates, and chlorides of magnesium, calcium, and sodium or more correctly, it will contain the corresponding ions. After treatment it will contain sulfate and chloride of sodium and the slight amount of calcium carbonate and magnesium hydroxide corresponding to the solubilities of these compounds, which is so small that it may be neglected.

Enough sodium carbonate is added so that the total of the sodium ion originally present plus that added shall equal in equivalents the sulfate and chlorine ion present in the untreated water. Calcium hydroxide is added in sufficient amount to neutralize any free acid, to change all the hydrocarbonate ions to carbonate and to precipitate the magnesium as hydroxide.

What promises to become an important method for softening water is based upon the fact that when a hard water is filtered slowly through a bed of artificial zeolite, $NaAlSiO_4 \cdot 3H_2O$, called "permutite" the calcium, magnesium, manganese, and iron are automatically removed and replaced by sodium from the zeolite. The filtering medium becomes exhausted, but may be rejuvenated by treatment with a strong solution of sodium chloride which reverses the action and dissolves the calcium, magnesium, etc., replacing them by sodium.

Zinc

General.—Starting with beryllium, zinc is the third member of the magnesium sub-group. It does not occur as abundantly in nature as magnesium, but is of far more importance technically. The world's annual production of metallic zinc is about 880,000 tons, of which the United States furnishes about 30 per cent. Kansas, Missouri, Wisconsin and New Jersey are the chief zinc producing states.

Occurrence.—The principal ores of zinc are the sulfide, ZnS, known as sphalerite, blende, rosin-jack, or black-jack; the carbonate, $ZnCO_3$, called smithsonite, zinc spar and sometimes, though improperly, calamine; the silicates, calamine, $Zn_2H_2SiO_5$ and willimite, Zn_2SiO_4; and franklinite, $(FeZnMn)(FeO_2)_2$.

Metallurgy.—The ores are first concentrated by crushing and washing away the lighter rock materials with water or in the case of the sulfide, by the recently devised flotation process which is rapidly increasing in popularity. In the latter process the ore is finely crushed and thoroughly churned up with air, oil and water. The ore particles, oil glob bbles of air unite to form an aggregate which is lighter than water and so floats off as froth while the worthless rock sinks to the bottom. The ores which contain the silicates or oxides of zinc merely require drying to remove the water before they are ready for reduction, but the carbonate should and the sulfide must be converted into the oxide before further treatment. The carbonate changes to the oxide when heated oderate temperature, being like magnesium carbonat spect. The sulfide must be roasted in the presence of the oxide and sulfur dioxide are formed:

$$2ZnS + \qquad O + 2SO_2$$

A part of the sulfur dioxide s ced is used to make sulfuric acid, and now furnishes 0 tons of this substance per year.

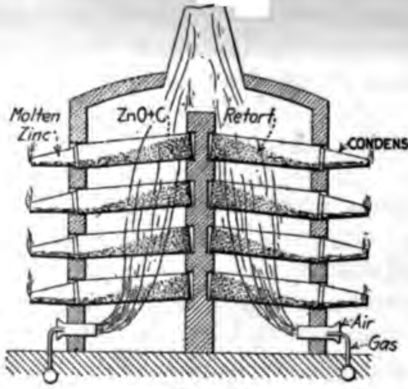

FIG. 58.

After getting the zinc in the form of anhydrous silicate or oxide, the next step is to reduce with carbon in a fire-clay retort furnace, Fig. 58. The equation for the chief reaction is

$$ZnO + C = Zn + CO$$

The temperature of reduction is about 1200°, while the boiling-point of zinc is 906°; hence, the zinc will be vaporized as rapidly as formed, and provision must be made to catch and condense the vapors.

When the condenser is cold, that is below 419°, the melting-t of zinc, the metal collects in the form of a fine powder which ains a few per cent. of the oxide, and is known as zinc dust; i it is above 419°, the zinc collects in the liquid state and is ed off and cast into moulds forming what is known as spelter. nder the best working conditions, the loss is great, as indi- l by the bluish-green color of the flames burning at the ths of the condensers, and the great amount of zinc oxide s which are given off and lost. An electrolytic process has ntly been developed to the commercial stage in this country. ore is roasted at a low temperature which produces ZnO $ZnSO_4$. The product is extracted with dilute sulfuric acid, the resulting impure solution of zinc sulfate is purified and electrolyzed, the zinc being deposited at the cathode. It ore than 99.99 per cent. pure and commands a premium on unt of its purity.

ysical Properties.—A fresh surface of pure zinc is brilliantly e, but quickly tarnishes and then has the familiar bluish- tinge. It melts at 419° and boils at 906°. Cast zinc is alline and very brittle, but when heated to between 100° 150°, it becomes malleable and may be rolled into thin sheets awn into wire. At about 200° it again becomes brittle and be powdered in a mortar. The density of the cast zinc is t 6.93 and of the rolled 7.18.

emical Properties.—Zinc belongs to the more active of the ents, but is far less so than the alkali or alkaline earth ls. It is not affected by dry air at ordinary temperatures, burns brilliantly above 500°. In ordinary air which contains r vapor and carbon dioxide, it quickly becomes covered a basic carbonate which acts as a protective coating and s the rest of the metal from further corrosion.

e behavior of zinc toward dilute sulfuric acid is very peculiar at while the commercial metal dissolves easily, very pure is not attacked until it is touched by a piece of copper, num, carbon, etc., then the evolution of hydrogen begins, on the copper, etc., and not on the zinc. However, the zinc s into solution while the copper is unchanged. The explana- is found in the fact that it is very difficult for hydrogen as o change to hydrogen gas at the surface of zinc; so much so the action is prevented with the pure metal. But if copper is in contact with the zinc, the change of hydrogen as ion to hydrogen gas takes place easily on the copper, and the positive charges of the hydrogen ion are conducted from the copper to the zinc and change the latter into the zinc ion.

Sodium or potassium hydroxide will slowly dissolve zinc forming hydrogen and zincate:

$$2] \qquad {}_2ZnO_2 + H_2$$

Zinc is used in vhich is 63 to 70 per cent.
copper and 37 to c; in many other alloys; in
electric batteries; an galvanizing iron.

Galvanized Iron.– the zinc produced per year
goes into galvanized iron coated with a layer of
zinc. This resists e weather better than plain
iron, because the zin t and so protects the iron.
The iron is coated with ways: first, by dipping very
clean sheets of iron into molten zinc; second, by electrically depositing zinc upon cathodes of iron from properly prepared solutions of zinc salts; third, by the process known as sherardizing, which consists in exposing the cleaned iron object to the vapors of metallic zinc. In some ways this last method has the advantage, because the zinc and iron adhere better than they do by the other methods.

Zinc Oxide and Hydroxide.—Zinc oxide, ZnO, or zinc white, is by far the most important manufactured compound of zinc, and is prepared on a very large scale, 59,000 tons per year, either directly from the ores or from the metal. In this country the ores are used exclusively and the process is briefly as follows: the ore, either franklinite or roasted sulfide, is mixed with anthracite coal and charged into a furnace upon a brisk fire of hard coal with a good draft of air; the zinc oxide is reduced, the metal volatilizes, and then is reoxidized, forming a very fine white powder which is carried along with the flue gases until well cooled, and is then collected in cloth bags which act as filters. The product is used as a pigment in paints, in rubber goods, as a starting point for the manufacture of other zinc compounds, and as a base for ointment in medicine. Its largest single use is in paints. It is not as poisonous as white lead, and does not blacken with hydrogen sulfide. A paint containing zinc oxide as the ly pigment gets very hard and brittle, so it is unsuited for terior work; but a mixture of white lead (basic lead carbonate) d zinc white is a great favorite and lasts better than either one. Rubber goods consume a great deal of zinc oxide, tomobile tires alone are said to require 40,000,000 lb. a year.

Zinc oxide is yellow when hot and white when cold. The ange is due to a shift in the region of the absorption of light om the invisible to the visible part of the spectrum.

The hydroxide is not formed by the combination of the ide and water, but may be obtained by adding a soluble ase to a zinc salt. It is a white difficultly soluble substance hich dissolves either in acids or in an excess of sodium or otassium hydroxide. This is due to the fact that zinc hydroxide ot only yields zinc and hydroxyl as ion, but also dissociates give hydrogen and zincate, ZnO_2^{--}, ions:

$$\underset{c_1}{Zn^{++}} + \underset{c_2}{2OH^-} \rightleftarrows \underset{c_3}{Zn(OH)_2} \rightleftarrows \underset{c_4}{2H^+} + \underset{c_5}{ZnO_2^{--}}$$

This action is typical of a number of hydroxides and hence lls for a rather full explanation. We have in these cases simulneous and dependent equilibria between the hydroxide and the o sets of ions. The mass law equations in this case are

$$\frac{c_3}{c_1c_2^2} = K \text{ and } \frac{c_4^2c_5}{c_3} = K'$$

an acid is added, its hydrogen ion will combine with the droxyl and thus reduce c_2 and hence decrease c_3 making the lution unsaturated and causing $Zn(OH)_2$ to dissolve and ineasing c. If on the other hand, a strong base is added the droxyl from the base will combine with the hydrogen ion from e zinc hydroxide and hence reduce c_4 thus causing c_3 to deease and the precipitate to dissolve to form a solution containing ncate ion, ZnO_2^{--}.

Zinc hydroxide is also soluble in excess of ammonia, due to the rmation of a complex zinc ammonia ion,

$$Zn^{++} + 2OH^- + nNH_3 = Zn(NH_3)_n^{++} + 2OH^-$$

Zinc Chloride.—Zinc chloride, $ZnCl_2$, may be made by the comnation of the elements; by the action of hydrochloric acid zinc, or on the oxide or the carbonate. It is a white, very deliquescent substance, which has a caustic action on the tissues. When a concentrated solution of the salt is mixed with zinc oxide, the whole sets to a hard mass of the oxychloride, $Zn(OH)Cl$, hence the mixture is used as a cement. Solutions of the chloride have been successfully employed in the treatment of wood to prevent decay and in other cases as an antiseptic and a deodorant.

Zinc chloride eithe [illegible] r in the fused state has the power of dissolving the [illegible] he metals; so it is used as a flux in soft soldering t [illegible] urfaces to be joined by the solder.

Zinc Sulfate.—Zinc su [illegible] $\cdot 7H_2O$, occurs in a hydrated form in nature to a s [illegible] It is known commercially as zinc vitriol or white v [illegible] ay be prepared by the action of sulfuric acid on zinc [illegible] allic zinc or by very careful roasting of ZnS. It is a [illegible] t, very soluble in water. It finds considerable use in medicine [illegible] dyeing, in the manufacture of glue, and in the preparation of a zinc sulfide and barium sulfate mixture known as lithophone which has been used as a white pigment, but is not durable.

$$BaS + ZnSO_4 = BaSO_4 + ZnS$$

Zinc Carbonate.—Zinc carbonate, $ZnCO_3$, occurs in nature as smithsonite and is of considerable importance as an ore of zinc. A basic carbonate is precipitated upon the addition of a soluble carbonate to a solution of a zinc salt. The term basic salt is applied to a mixed salt containing hydroxyl or oxygen and some other anion; frequently the basic salts are mixtures of the hydroxide or oxide with the other salt, but very often they are true chemical compounds.

Zinc Sulfide.—The occurrence of zinc sulfide, ZnS, in nature has already been discussed. It is commonly known as blende and in its pure state is nearly white, but it shades to brown and even black depending upon the impurities it contains. It may be precipitated by the addition of ammonium sulfide or hydrogen sulfide to solutions of zinc salts. In this form, it is a fine white amorphous powder and is used as a pigment. Of the ordinary heavy metals, zinc is the only one that forms a white sulfide. It is soluble in dilute acids, and hence must be precipitated from neutral solutions. If the precipitation is to be complete, the concentration of the hydrogen ion must be kept low. This may be done by adding an acetate to the solution. Most of the hydrogen is withdrawn in this way from the solution to form undissociated acetic acid. Zinc sulfide is infusible and very difficultly volatile. Its most important use is in the extraction of the metal.

Analytical Properties of Zinc.—Analytically, zinc is in a group with manganese, nickel and cobalt. These all have the common property of being precipitated as their sulfides by ammonium sulfide, but not by hydrogen sulfide in acid solution. Zinc and manganese sulfides are soluble in dilute sulfuric acid, while cobalt and nickel sulfide are practically unaffected. Zinc is distinguished from manganese by the fact that its hydroxide is soluble in an excess of potassium hydroxide, while that of manganese is not. From this alkaline solution, hydrogen sulfide will reprecipitate white zinc sulfide. The color of the sulfide is very characteristic, for it is the only common sulfide of a heavy metal which is white. The facts that the oxide is yellow when hot and white when cold, and that a green mass is formed when the oxide is wet with cobalt nitrate solution and then strongly heated are used in analytical work.

CADMIUM

Cadmium is an element which is very closely allied to zinc in its properties and is found in nature in comparatively small amounts associated with this metal. The boiling-point of cadmium is much lower than that of zinc, consequently it is present quite largely in the first portions of the distillate obtained in the preparation of the latter metal. It may be freed from the zinc by repeated distillations at as low a temperature as possible, in an atmosphere of hydrogen to prevent its oxidation. This product may be further purified by electrolysis, a solution of $CdSO_4$ being used as the electrolyte.

The element thus obtained is a bluish-white soft metal of a crystalline structure, density 8.64, melting at 321° and boiling at 766°. The molecular weight as determined from the vapor density is very nearly 112.4, the number which represents the atomic weight, consequently the f [illegible]d.

and in the extraction of gold and silver from their ores, since it readily forms amalgams with these metals. Amalgams, as the alloys of mercury are called, are formed by nearly all of the metals. Iron and platinum are generally exceptions, but even these may be amalgamated under special conditions.

Pure mercury does not wet glass but runs around on it in clean round drops. When it contains even a small quantity of foreign metal it becomes cove [illegible] of oxide and then when it runs on glass, it strings [illegible] tail. This is a fairly sensitive test for impurities [illegible].

It is interesting to n [illegible] y is the only metal which is liquid at ordinary t [illegible] although cesium melts at temperatures which ar [illegible] during the summer.

Chemical Properties.– [illegible] not oxidize upon exposure to the air at ordinary [illegible] but does so very slowly at about 300°, forming [illegible] This fact was of great importance in the developmen [illegible] he present conception of combustion. (See p. 16.)

Mercury combines readily with sulfur and the halogens. It is not attacked by dilute hydrochloric or sulfuric acids, since the hydrogen as ion from these is not a strong enough oxidizing agent to oxidize the mercury to ion. It is dissolved by nitric acid or by hot sulfuric acid with the reduction of a part of the acids, and the evolution of nitric oxide or sulfur dioxide instead of hydrogen.

The compounds of mercury which are soluble enough to be absorbed by the human system are decidedly poisonous, but mercury in large drops is not. If, however, the mercury is very finely divided as it is in "blue mass" or in the form of vapor it exhibits its poisonous action. Mercury compounds are extremely poisonous toward bacteria and enough of the metal dissolves in pure water to kill these organisms in a short time. Mercury forms two series of compounds. In the one, it is divalent; and in the other it is at least apparently monovalent. The monovalent compounds are called mercurous and the divalent mercuric salts, and it is through the latter that the element establishes its connection with the magnesium group. The mercurous compounds will be discussed first.

MERCUROUS COMPOUNDS

ercurous Oxide.—Mercurous oxide, Hg_2O, is a blackish-wn substance which is formed by the action of an excess of um or potassium hydroxide upon a mercurous salt. It is not ble in water and is very unstable, breaking down under the on of light or moderately high temperature into mercury and curic oxide. Mercurous hydroxide is unknown.

ercurous Chloride.—Mercurous chloride or calomel, $HgCl$ or Cl_2, is the most important mercurous salt. It is very diffi-ly soluble in water and may be precipitated by adding a tion containing chlorine ions to a solution of mercurous ate. It is usually prepared by subliming a mixture of curic chloride, $HgCl_2$, and mercury,

$$HgCl_2 + Hg = 2HgCl$$

ercurous chloride or calomel is largely used in medicine ause it stimulates the liver and other organs producing the etions. The vapor pressure of mercurous chloride reaches atmosphere below the melting-point, and therefore the stance sublimes. Unless very pure, it should be protected m light which decomposes the ordinary salt, forming mercury l mercuric chloride which is very poisonous.

Mercurous Bromide.—Mercurons bromide, $HgBr$, is precipi-ed, as a white powder, by adding a bromide to mercurous rate.

Mercurous Iodide.—Mercurous iodide, HgI, may be formed ectly from the elements or by precipitation from mercurous rate by an iodide. It is unstable and changes into mercury l mercuric iodide. The change takes place easily in the sence of an excess of KI, since the latter dissolves the mercuric ide formed.

ercurous Nitrate.—Mercurous nitrate, $HgNO_3 \cdot H_2O$, is the st important soluble mercurous salt. It is made by acting n an excess of mercury with cold dilute nitric acid. It lrolyzes, forming a basic nitrate, $Hg_2(OH)NO_3$, which is but htly soluble. Hence, a clear solution of the salt must contain ic acid. Some metallic mercury should be kept in the solu-n to reduce any mercuric ion which might form,

$$Hg + Hg^{++} = 2Hg^{+}$$

Mercurous Sulfate.—Mercurous sulfate, Hg_2SO_4, may be pr pared by the action of hot-concentrated sulfuric acid upon excess of mercury, or by adding the dilute acid to a mercuro nitrate solution. It may also be obtained by the electroly of dilute sulfuric acid using mercury as anode. It is white a but slightly s ut more so than the chlorid It is used in the andard cells for the comparis of electromotive

Mercurous Sı s sulfide, Hg_2S, is very unsta and can exist c ures below −10°; at ordin temperatures it mercuric sulfide and mercur

OMPOUNDS

Mercuric Oxide.—Mercuric . xide or red precipitate, H is usually prepared by heating an intimate mixture of merc nitrate and mercury until no more red fumes of nitrogen perox are given off.

$$Hg(NO_3)_2 + Hg = 2HgO + 2NO_2$$

When a solution of potassium or sodium hydroxide is ad to a mercuric salt, a yellow precipitate of very finely divi mercuric oxide is formed. This precipitate is more act chemically and therapeutically than the coarser red oxide.

When mercuric oxide is heated it darkens, becoming alm black, and at a red heat it is decomposed into the elements. will be recalled, it was through this reaction that Priestly covered oxygen. Mercuric oxide is very poisonous, but is u in medicine.

Mercuric hydroxide is so unstable that it has not yet b prepared. The mercuric salts of the oxy-acids are hig hydrolyzed, so it must be a very weak base.

Mercuric Chloride.—Mercuric chloride or corrosive sublim $HgCl_2$, may be made by the direct combination of the eleme at a slightly elevated temperature. The combination takes pl with a peculiar green flame.

The salt is usually obtained as a crystalline sublimate heating a mixture of mercuric sulfate, common salt, and a li

ganese dioxide, the latter being added to oxidize any mer-
us sulfate which may be present.

is much more soluble in hot water than in cold. It is soluble
lcohol and ether and a number of other organic solvents.
aqueous solution is slightly acid, indicating some hydrolysis,
no basic salt is deposited as is the case with mercuric nitrate
sulfate. The explanation for this is furnished in the fact
as indicated by the electrical conductivity, the halogen
pounds of mercury are but slightly ionized, while the sulfate
nitrate and the salts of other oxyacids are strongly disso-
ed. The inevitable results of this would be that the mercuric
s of the oxyacids would hydrolyze further than the halides.
his connection it will be recalled that the halogen compounds
admium were less dissociated than the salts of the oxyacids.
lercury compounds are highly poisonous to all forms of life,
mercuric chloride is much used as an antiseptic. For this
pose it is often put up in tablets with sodium chloride which
kes it dissolve more rapidly. It is used in medicine both
rnally and externally, but because of its highly poisonous
ure must be used very cautiously. Its antidote is white of
, with which it forms a difficultly soluble compound. This
uld be removed by a stomach pump and magnesium sulfide
ninistered to precipitate the last traces of mercury.

Mercuric Bromide and Iodide.—Mercuric bromide, $HgBr_2$, is
ch like the chloride, but is less soblule in water; it is also less
sociated than the chloride. Mercuric iodide, HgI_2, is but
htly soluble in water and is formed as a yellow precipitate
ich rapidly becomes scarlet when a solution of an iodide is
ded to a solution of a mercuric salt. It dissolves freely in
ution of potassium iodide forming a colorless very soluble
aplex salt, K_2HgI_4, which fails to give most of the reactions
mercury; for example, potassium hydroxide does not pre-
itate mercuric oxide. After the addition of potassium hy-
xide, the solution is called Nessler reagent, and is very
sitive toward ammonia which gives a yellow precipitate hav-
the formula $Hg_2NI \cdot H_2O$.

Mercuric iodide exists in the two forms; the scarlet, stable
m ordinary temperatures to 126°, and the yellow, stable
ove this temperature up t[illegible]lting-point, 253°.

Mercuric iodide and its complex potassium salt are u medicine.

Mercuric Nitrate.—Mercuric nitrate, $Hg(NO_3)_2$, is prepa dissolving the metal in hot nitric acid, and boiling until a p of the solution does not yield a precipitate of mercurous c upon the addition of a chloride. It forms colorless ver quescent crys omposition $Hg(NO_3)_2 \cdot H_2O$, soluble in wate hydrolyzed, precipitating a basic salt.

Mercuric Sulfate. ercury is heated with concen sulfuric acid, mer $HgSO_4$, water, and sulfur are formed. The fate so obtained is a white c line salt which is e in water containing sulfuri but hydrolyzes in r forming a yellow basi $Hg_3(SO_4)O_2$.

Mercuric Sulfide.—The most stable compound of m is the sulfide, HgS. This exists in the two forms, black phous and red crystalline. The latter occurs in nature nabar and is the most important ore of mercury. As is t eral rule, the amorphous form is the less stable and th soluble of the two, but both are exceedingly slightly substances. The black form is precipitated whenever hy sulfide or a soluble sulfide acts upon a mercuric salt. It i what soluble in sodium and potassium sulfide forming in t of the sodium sulfide a white crystalline salt, Na_2HgS From this solution the less soluble red crystalline form is gr deposited. The red crystalline modification may also tained by subliming the black. The artificial red sul called vermilion and is used as a pigment.

Both forms of mercuric sulfide are very stable and a attacked by hydrochloric acid or by dilute nitric acid cold. The compound is dissolved by aqua regia, the sul being liberated as free sulfur or oxidized to the sulfate. curic sulfide is the most stable sulfide of the metals and utilized in the analytical separation and identification metal.

Mercuric Cyanide.—Mercuric cyanide, $Hg(NC)_2$, the halogen compounds of mercury in many ways.

soluble than the halides, but is even less dissociated than these, and its solution is a very poor conductor of electricity.

When heated, mercuric cyanide decomposes into mercury and cyanogen, C_2N_2,

$$Hg(NC)_2 = Hg + C_2N_2$$

and this furnishes a very convenient method for the preparation of cyanogen.

Mercury Fulminate.—When mercury is dissolved in hot nitric acid and alcohol added to the still hot solution, a white precipitate of mercury fulminate, $Hg(ONC)_2$, is soon formed. This, when dry, explodes upon being struck, and is used in percussion caps and in the caps for exploding guncotton and dynamite.

Complex Compounds of Mercury.—Mercury forms a very large number of complex compounds far too large for them all to be considered in detail or even mentioned in a book of this kind. The nitrogen compounds, however, demand a little attention.

Mercuric Ammonia.—The mercuric salts react with ammonia to form compounds which may be grouped into three classes: first, those with ammonia of crystallization similar to salts with water of crystallization; second, ammono basic salts analogous to ordinary basic salts with NH_2 in place of OH or either NH or N in place of O; third, mixed aquo ammono basic salts containing both OH or O and NH_2 or N.

The first class with ammonia of crystallization may be prepared by the action of ammonia in the gaseous or liquid state upon mercuric salts, or by the action of aqueous ammonia upon these salts in the presence of ammonium salts. As examples of these compounds the following may be given: $HgCl_2 \cdot 2NH_3$ [fusible white precipitate], $HgCl_2 \cdot 12NH_3$.

The second class, ammono basic mercuric salts, may be formed by the action of aqueous ammonia upon mercuric salts in the absence of ammonium salts. Examples of these salts are $HgNH_2Cl$ [infusible precipitate], and $Hg(NH_2)NO_3$.

The third class, the mixed aquo ammono basic salts, are formed under conditions which are more favorable to hydrolysis than those for the two preceding classe [illegible] ound $Hg_2(OH)(NH)C$ [illegible] an exampl

Analytical Reactions of Mercury.—Both the mercurous and mercuric ions are colorless, and the former is distinguished from all others by the fact that it will form a slightly soluble white precipitate of mercurous chloride with the chlorine ion which precipitate turns black when treated with ammonium hydroxide. Both the mercuric and mercurous ions give mercuric sulfide with hydrogen s[illegible]ution. This precipitate is insoluble in hot dilu[illegible]t is dissolved by aqua regia. Mercuric salts are r[illegible]nous chloride to mercurous salts or even metall[illegible]vn in the following equations,

$2HgC$ [illegible] $IgCl + SnCl_4$

and

HgC [illegible] $Ig + SnCl_4$

When metallic copper is [illegible] into a solution of a mercury salt the copper is oxidized to copp[illegible] as ion and the mercury ion is reduced to metallic mercury which forms a bright mirror-like coat on the remaining copper.

When the mercury salts are heated with lime or sodium carbonate, they give metallic mercury.

General Relations of the Group.—As is evident from the discussion given above, the members of the magnesium group do not form as close a family as do the members of the alkali and alkaline earth metals, but still there are some general relationships throughout the group. The increasing stability of the sulfides with increasing atomic weight is noticeable. Beryllium and magnesium sulfides are not formed in the presence of water even, while zinc sulfide is stable toward weak acids, but is not stable in contact with any but very dilute solutions of the strong acids. Cadmium sulfide is stable in the presence of dilute solutions of the strong acids, but is dissolved by concentrate solutions of them and by hot dilute solutions, while mercuric sulfide is stable even against boiling dilute nitric acid and is scarcely attacked by this acid in the concentrated state.

Beginning with zinc, the halogen compounds show a regular decrease in their degree of dissociation with increasing atomic weight both of the halogen and of the metal. The melting- and boiling-points of the members of the sub-group become lower as the atomic weights increase.

CHAPTER XXIV

COPPER, SILVER AND GOLD

eral.—Copper, silver, and gold occupy the lower part right-hand column of Group I of the periodic system. their position, they should bear some resemblance to the metals, but from what has been learned concerning the ns between the members of the alkaline earth metals and sium sub-group it is evident that the resemblance need not e. As a matter of fact the divergence is so great that it is ary to search for points of resemblance. Perhaps the striking point of similarity is that copper, silver and gold orms a series of compounds in which it is monovalent. In on copper forms another series in which it is divalent and ne in which it is trivalent. The following table will give ance a comparison of the more prominent properties of the b-groups:

The Alkali Metals	The Copper Family
nsity 0.59–2.4.	High density 8.94–19.4.
tive chemically.	Decidedly inactive.
ccur free.	Often found free.
n compounds are soluble.	Nearly all of the halogn compounds of the monovalent series are but slightly soluble.
bases.	Weak bases, except silver.
form complex ions.	Form many complex ions.

Copper

tory.—Copper has been known from prehistoric times and t is found free in nature in abundance, it was probably the etal to be put to practical use by man. Before the ex- e use of iron, tools were made of bronze, an alloy of copper n.

urrence.—Copper occurs in nature both free and in com- n. The native copper is sufficiently abundant so that it constitutes a very important ore as may be judged from the fact that the region in Michigan near Lake Superior produces from the native metal about one-sixth of the copper mined in this country per year. The compounds which are used as ores may be divided into two classes: the oxidized ores and the sulfide ores. The oxidized ores include cuprous oxide, Cu_2O, which is called cuprite or red oxi CuO, called melaconite or black oxide; and t rbonates, malachite, $CuCO_3\cdot$ $Cu(OH)_2$, and a $Cu(OH)_2$. The sulfide ores cuprous sulfide, Cu_2S, or e and the double sulfides of nd iron known as chalcopy- eS_2, and bornite, Cu_3FeS_3. de ores are the most impor- use from them this country about two-thirds of its out- pu year. The total production in 1915 was nearly 1,425,000,000 lb.

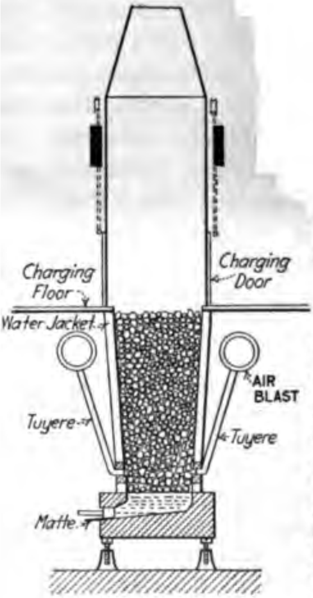

FIG. 59.

Metallurgy.—The method adopted for the extraction of copper from its ores naturally depends upon the substances present. If the copper is native, all that is necessary is to crush the rock and concentrate the copper by mechanical processes followed by melting in large reverberatory furnaces to separate the copper from the remaining gangue. If the ore is a sulfide it is crushed and concentrated by washing and flotation as described under zinc. The latter process is so effective that from an ore running as low as 2 per cent. copper 90 to 96 per cent. of the metal can be obtained in the concentrate.

The first step involved in the actual smelting of the ore is the formation of a concentrated mixture of copper and iron sulfide known as copper matte. This is done by melting a properly proportioned mixture of the concentrated ore and limestone either in a reverberatory furnace, if the ore is in fine particles, or in a copper blast furnace if it is coarse. In either t furnace part of the iron sulfide is oxidized to sulfur dioxide and iron oxide and the latter together with lime from the limestone and silica from the ore forms easily fusible silicates or slags, the remaining iron sulfide and the copper sulfide melt together forming the matte and when the charge is withdrawn from the furnace, the matte goes to the bottom of the receiving vessel and is easily separated from the slag. In the reverberatory furnace, the ore and limestone are spread on the horizontal bed of the furnace and exposed to the action of the flame produced by blowing powdered coal into the furnace with a blast of air; while in the copper blast furnace the ore and flux together with coke for fuel is charged into the top of the long narrow vertical furnace (Fig. 59) into which air is blown at the bottom. The temperature reached is high and the molten slag and matte are drawn off at the bottom. The matte from either type of furnace is next treated in a copper converter (Fig. 60), which is a large, approximately barrel-shaped vessel resting on a rotating mechanism. The converter has a thick lining of magnesia, MgO. Air at a high pressure is blown into the converter from several blast pipes on the side.

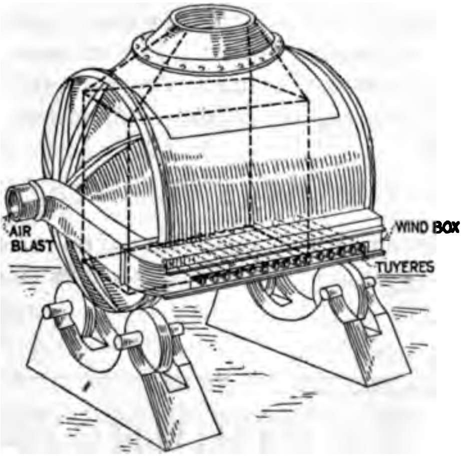

FIG. 60.

The large supply of air, oxidizes the ferrous sulfide in the matte to iron oxide and sulfur dioxide, thus liberating heat which serves to keep the mass fluid.

$$2FeS + 3O_2 = 2FeO + 2SO_2$$

The sulfur dioxide escapes as gas, while the ferrous oxide combines with silica which is added along with the matte to form ferrous silicate slag,

$$FeO + SiO_2 = FeSiO_3$$

Some cuprous sulf t the cuprous oxide formed reacts at once with ning cuprous sulfide,

2Cu $_2O + 2SO_2$
Cu $S + FeO$

After the iron has be e slag is poured off and the second period of b The cuprous sulfide is now oxidized to some uprous oxide. This reacts with the remaining forming sulfur dioxide and metallic copper

$$Cu_2S + 2Cu_2O = 6Cu + SO_2$$

At the completion of this operation metallic copper remains and this is poured into molds. It is known as blister copper and carries practically all of the nickel, gold, silver, and platinum that were in the original ore. It also contains some other impurities and is not fit to be used for most commercial purposes. Further purification is best obtained by means of electrolysis.

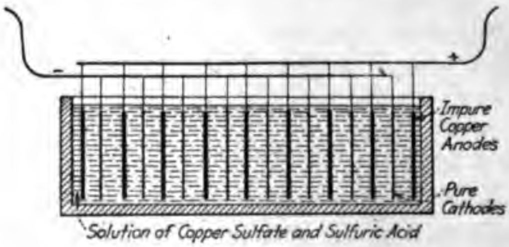

FIG. 61.

Electrolytic Refining.—For this process, the crude blister copper is cast into large plates which are used as anodes in electrolytic cells (Fig. 61) where the cathodes are thin plates of pure copper, and the electrolyte is an acidified solution of copper

On passing a suitable current through the cells, is dissolved from the impure anodes and deposited ly pure condition on the cathodes. The impurities in de are either dissolved and held in solution in the elec- or remain undissolved and fall to the bottom of the cell. ilver and platinum are thus precipitated and are recovered equently melting up the slimes or mud from the bottom ells. The electrolytic copper so obtained is nearly pure. lted again, stirred with wooden poles to remove oxide and st into bars for the market.

ical Properties of Copper.—Copper is red by reflected d is one of the very few colored metals. When a very yer of copper is viewed by transmitted light it is bluish- The density of the metal is 8.94 and it melts at 1,083° ils at 2,310°. The metal is a very good conductor of heat y silver exceeds it in conductivity for electricity. A large ion of the copper which is put upon the market is used for al conductors. For this purpose it must be extremely It is highly malleable, ductile and tenacious, so it may d or hammered into thin sheets or drawn into fine wire.

ical Properties.—Copper is not oxidized in perfectly dry in ordinary air it soon becomes coated with an adherent cuprous oxide and finally, especially if exposed to the r, with a basic carbonate. The underlying metal is ghly protected by these films and is very durable. On ount, it is used for the roofs of important buildings and eathing for ships. At somewhat elevated temperatures combines directly with oxygen, chlorine, and sulfur. not act on water at any temperature and is not dissolved ls with evolution of hydrogen. This is connected with t that the cupric ion is a stronger oxidizing agent than rogen ion. Such acids as contain elements in a condition makes them stronger oxidizing agents than hydrogen as tric or hot concentrated sulfuric acid for example, will copper but with the reduction of the acid and not the n of hydrogen. On the other hand, when in contact e air, acids like hydrochloric and even acetic dissolve the The oxygen of the air is the oxidizing agent in this case. atomic weight of copper is 63.57.

Alloys.—Copper forms many varied and useful alloys with the other elements. With zinc it forms brass, 30 to 37 per cent. zinc, and tombac 2 to 15 per cent. zinc, and with zinc and iron, an alloy which is malleable when hot. Bronze contains essentially copper and tin, although other metals are often added, especially zinc. Gun metal contains 10 per cent. tin and bell metal from 17 to 20 per cent. tin. Speculum metal is one-third tin and contains a little arsenic. It takes a very high polish. Phosphor bronze contains tin and a little phosphorus. Aluminum bronze has from 3 to 10 per cent. of aluminum. That with the higher percentage of aluminum has about the color of gold, is easily cast, takes a high polish and is nearly as strong as cast steel. Manganese bronze has a content of about 30 per cent. manganese. Silicon bronze contains up to 5 per cent. silicon. It is sometimes used for exposed electric wires since its tenacity is greater than that of copper although its conductivity is smaller. German silver is an alloy of copper, nickel and zinc and usually contains about 22 per cent. each of zinc and nickel.

Cuprous Compounds.—The cuprous or monovalent compounds are formed as the first step in the oxidation of the element or in the reduction of the cupric, or divalent compounds. In some ways many of them are more stable than the cupric compounds, and are formed from the latter by spontaneous decomposition; but in general they are relatively unstable and are transformed by oxidizing agents into the cupric compounds. The principal cuprous compounds are Cu_2O, CuCl, CuBr, CuI, CuNC, and Cu_2S. Some of the cuprous oxyacid salts can be obtained in solution, but they soon decompose in such a manner that half the cuprous is reduced to metallic copper while the other half is oxidized to cupric. The cuprous ion Cu^+ seems to be incapable of existing in any appreciable concentration for all the soluble stable salts are those of complex ions.

When a given quantity of electricity is passed through a cuprous salt, just twice as much copper is deposited as when the same quantity is passed through a cupric solution. This of course, would follow from the relation between their valencies.

Cuprous Oxide.—Cuprous oxide occurs in nature and is known as cuprite or red oxide of copper. It may be prepared the direct union of the elements, or by the reduction of an aline solution of a cupric salt with glucose. It has a red r and is not soluble in water. It dissolves in hydrochloric d forming the compound, $HCuCl_2$ which gives the complex $CuCl_2^-$; and in ammonium hydroxide owing to the formation he complex ion $Cu(NH_3)_2^+$. Both of these ions are colorless. prous hydroxide is not stable.

uprous Chloride.—Cuprous chloride, CuCl, is one of the most portant of the cuprous salts. It is most readily prepared by ding hydrochloric acid to a solution of cupric chloride, $CuCl_2$, d boiling for some time with finely divided copper out of ntact with air. The equation for the reaction is:

$$CuCl_2 + Cu + 2HCl = 2HCuCl_2$$

hen the solution is poured into water, the compound $HCuCl_2$ eaks up,

$$HCuCl_2 \rightleftarrows HCl + CuCl$$

prous chloride is white and is but slightly soluble in water. is dissolved by concentrated hydrochloric acid and soluble lorides in general through the formation of the complex ions Cl_2^- or $CuCl_3^{--}$. These solutions are colorless when pure, t quickly become colored when exposed to the air, owing to e oxidation to cupric compounds. Cuprous chloride is also luble in ammonium hydroxide solutions owing to the formaon of the colorless ion $Cu(NH_3)_2^+$. The solution, however, ickly turns blue upon exposure to the air because of oxidation the highly colored cupric ammonia ion.

Both the ammoniacal and hydrochloric acid solutions of prous chloride have the property of absorbing carbon monoxide rough the formation of an unstable compound. Advantage is ken of this in gas analysis.

uprous Bromide.—Cuprous bromide, CuBr, is very similar the chloride. It may be prepared by simply heating the hydrous cupric bromide out of contact with the air when it composes into bromine and the cuprous salt. The chloride ows a tendency in the same direction but the decomposition incomplete.

Cuprous Iodide.—Cupric iodide is so unstable that it decomses at ordinary temperatures even when in solution; so when a soluble iodide is added to a solution of a cupric salt, cup iodide is at once precipitated and iodine liberated,

$$2Cu^{++} + 4I^{-} \rightleftarrows 2CuI + I_2$$

The cuprous iodide is colorless but appears brown from color of the liberated iodine. The reaction is reversible ar far from complete unless the iodine is reduced by the addi of a sulfite or other suitable reducing agent.

Cuprous Cyanide.—When potassium cyanide is added cupric salt, cupric cyanide is precipitated; but this is unst and soon decomposes into the cuprous cyanide, CuNC, cyanogen,

$$2Cu(NC)_2 = 2CuNC + C_2N_2$$

The cuprous cyanide is practically insoluble in water, but solves readily in an excess of potassium cyanide owing to formation of the colorless very stable complex anion Cu(N This ion gives an exceedingly low concentration of copper as so low in fact, that it does not show the properties of copp ion and will not give a precipitate of copper sulfide (w see) with hydrogen sulfide. Because of the very small centration of the copper ion from this cuprocyanogen all the slightly soluble salts of copper will dissolve in an e of potassium cyanide.

Cuprous Sulfide.—Cuprous sulfide, Cu_2S, is formed by he the cupric compound in a stream of hydrogen. It is fou nature and is then known as copper glance. It is dark co and is not soluble in water or cold dilute acids, but is diss by hot dilute nitric acid and by potassium cyanide.

The Cupric Compounds.—The cupric compounds are div and are in general more common and more important tha cuprous. The halogen compounds, as noted in the discu of the cuprous salts, show a marked tendency to pass ove the cuprous salt and the free halogen. On the other hanc only stable oxy salts of copper belong to the cupric series. in dilute solution in water, the cupric salts all show a blue which consequently is said to be the color of the cupri Cu^{++}. When an excess of ammonium hydroxide is addec cupric salt, the precipitate of cupric hydroxide or basic salt

·st formed is redissolved and the solution becomes intensely ı. Such a solution acts as though it contained a complex ric ammonia ion, $Cu(NH_3)_4^{++}$, having a deep blue color.

upric Oxide and Hydroxide.—Cupric oxide or black oxide of per, CuO, occurs in nature in the ore melaconite. It may be pared by heating the metal in a stream of oxygen or air; ous oxide is first formed. When heated to redness, it acts good oxidizing agent toward hydrogen and organic subces, oxidizing them to water and carbon dioxide and being f reduced to metallic copper. This property is employed he quantitative synthesis of water and in the analysis of nic compounds. Copper oxide is also used in the refining etroleum to remove sulfur compounds.

upric hydroxide, $Cu(OH)_2$, is a weak base which is but ıtly soluble in water. It is precipitated as a light blue gelatıs substance when a soluble hydroxide is added to a cupric Upon standing or more quickly when the solution is ed, it becomes black and is transformed into a hydrated ı of the oxide.

upric hydroxide is of course soluble in acids. It is not dised by sodium hydroxide of moderate concentrations, but oluble in ammonium hydroxide owing to the formation of deep blue complex cupric ammonia ion $Cu(NH_3)_4^{++}$. It is soluble in solutions of sodium and potassium tartrate, espey in the presence of sodium hydroxide, a complex copper rate ion, $CuC_4H_2O_6^{--}$, is formed. This solution is deep blue the ammoniacal solution, and is used in the determination lucose since the latter reacts in a definite manner with it ıing cuprous oxide which is presipitated. It is called Fehls solution. This solution of cupric hydroxide in ammonia the remarkable property of dissolving cotton or other forms ellulose. This is reprecipitated upon acidulating the solution form having a silky luster. This is the basis of the process ıaking artificial silk.

upric Chloride.—Cupric chloride, $CuCl_2$, may be prepared he direct union of its elements or by the interaction of hydroric acid with the oxide, hydroxide, or carbonate.

nhydrous cupric chloride is yellow, a dilute solution of the is blue and a concentrated sol perhaps because of the simultaneous presence of the ion and of the undissociated salt. From the concentrated solution, the blue hydrate, $CuCl_2 \cdot 2H_2O$, crystallizes out.

The deep blue solution formed by the addition of an excess of ammonia to a solution of cupric chloride deposits upon concentration crystals having the formula $Cu(NH_3)_4Cl_2 \cdot H_2O$. The anhydrous chloride will combine directly with ammonia to form the compounds, $CuCl_2 \cdot 6NH_3$ and $CuCl_2 \cdot 2NH_3$, these are analogous to salts with water of crystallization.

Cupric Sulfate.—Copper sulfate or blue vitriol, $CuSO_4 \cdot 5H_2O$, is the most important copper salt. It may be made on a small scale by heating copper with concentrated sulfuric acid. The sulfuric acid here acts as the oxidizing agent, and is itself reduced to sulfur dioxide,

$$Cu + 2H_2SO_4 = CuSO_4 + SO_2 + 2H_2O$$

On a large scale, it is made by carefully oxidizing naturally occurring sulfides by roasting them in the air and dissolving out the sulfate with water, or by roasting the ores or matte and dissolving in dilute sulfuric acid. The salt is soluble in water, and crystallizes from solution as the blue pentahydrate, $CuSO_4 \cdot 5H_2O$. The five molecules of water of crystallization in the pentahydrate may be successively replaced by the same number of molecules of ammonia. A similar thing is true for other salts and serves to strengthen the resemblance between ammonia and water. With potassium sulfate, copper sulfate forms the double salt, $CuSO_4 \cdot K_2SO_4 \cdot 6H_2O$, isomorphous with the corresponding magnesium compound.

Copper sulfate is used in the preparation of other copper compounds, in calico printing, in the purification of copper by electrolysis, in electroplating and electrotyping, as a germicide and fungicide (mixed with slaked lime it forms Bordeaux mixture). Since it is very poisonous to the lower orders of plants, it is used extensively to destroy such organisms as often give to public water supplies a diasgreeable taste and odor. It is used in making the electric cell known as the Daniel's battery and also in the gravity battery.

Cupric Nitrate.—Copper nitrate, $Cu(NO_3)_2 \cdot 6H_2O$ is a blue salt which may be made by dissolving the metal, the oxide or onate in nitric acid. It is very easily soluble in water. :n heated it gives the oxide.

ıpric Carbonate.—Cupric hydroxide is such a weak base that normal carbonate does not seem to be able to exist since ıs neither been found in nature nor prepared in the labora- . Two basic carbonates, malachite, $CuCO_3{\cdot}Cu(OH)_2$ and ite, $2CuCO_3{\cdot}Cu(OH)_2$ occur fairly abundantly in nature and valuable copper ores. The green coating which gradually ıs on copper exposed to the weather has the composition of ıchite.

ıpric Acetate.—A basic copper acetate, known as verdigris ng a fine bluish-green color and used as a pigment, is formed ıe action of the air and of the crudest kind of vinegar (acetic) upon plates of copper. The oxygen of the air is the oxidiz- ıgent in this case. The normal salt, $Cu(C_2H_3O_2)_2{\cdot}H_2O$ may btained by crystallization from dilute acetic acid. It forms green crystals and is used as a pigment.

ıpric Sulfide.—When hydrogen sulfide is passed through a ral or acid solution of a cupric salt, a brownish-black pre- ate is thrown down; this consists principally of the cupric le, CuS, but always contains some cuprous sulfide, Cu_2S. lrying this precipitate and heating it in a current of hydrogen, completely transformed into the cuprous compound. The ·ogen assists by sweeping away the sulfur.

ıpric sulfide is practically insoluble in cold dilute acids, but ılves in hot dilute nitric acid. In the latter case, hydrogen le is not evolved; but the sulfur as ion is oxidized to free ır and the nitric acid reduced to nitric oxide.

ıpper Ferrocyanide, Osmotic Pressure.—Copper ferro- ide, $Cu_2Fe(NC)_6$ has a very intense brownish-red color is exceedingly slightly soluble. Because of these properties, of some importance to analytical chemistry. It is, however, r greater importance to biology and to theoretical chemistry, use of the part which it plays in the study of the phenomena ımotic pressure.

ıpper ferrocyanide is a colloidal substance, and may be ined as a membrane filling the pores of a porous cell (Fig. 62) ıutting a solution of copper sulfate on the inside of the cell a solution of potassium ferrocyanide on the outside and allowing the whole to stand for some time. The ferrocy precipitated in the pores of the cell where the two solution After this cell has been thoroughly washed to free it from salts, it behaves in a very peculiar manner. Pure wat pass through it in either direction very much as thro ordinary porous cell only more slowly; but if a solution c or of many other substances is placed in the cell, and th then set into a dish of pure water, the water will be drawn t into the solution. If the cell be closed cork, the water will continue to enter has produced a certain pressure which measured upon an attached manometer. this pressure is reached, the water ceases t and if by any means the pressure within is increased *pure water and not solution* i out of the cell until the pressure is red its former value. This pressure at whic is equilibrium between pure water and a s separated by a membrane such as coppe cyanide is called the osmotic pressure solution.

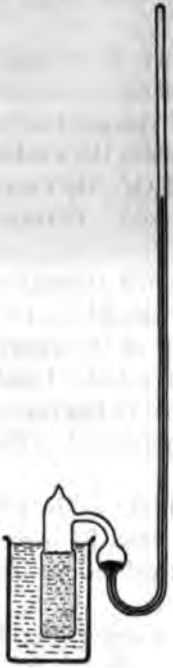

Fig. 62.

When the conditions which affect the pressure are investigated, it is found t fairly dilute solutions, the osmotic pre directly proportional to the concentratio solution and to the absolute temperature a it is measured. In these ways it corr exactly to the pressure of a gaseous sul *In fact, the osmotic pressure of a solutio same as the pressure which the solute wo if it were in the state of a gas and occu volume of the solvent in which it is dissolved at the temper which the osmotic pressure is measured.* The gas law eq $PV = K$ and $V = K'T$ apply to osmotic pressure also, I osmotic pressure, V the volume of the solvent (not the of the solution), and T the absolute temperature. The pressure of a solution containing one gram mole in a solvent is approximately 22.4 atmospheres at 0°C.

Other membranes than copper ferrocyanide may b out altering the value of the osmotic pressure of a solution ided always that they will permit the solvent to pass through, not the solute. Such membranes are called semipermeable branes. They seem to act as selective solvents and to lve the solvent but not the solute of the main solution. ie osmotic pressure of salt solutions is abnormally high ig about twice the calculated value, in the case of sodium ide, for example. The significance in connection with the ciation hypothesis is obvious, but really it adds nothing to evidence already given in favor of this theory, because the ce of thermodynamics has shown that the osmotic pressure solution is directly proportional to the relative lowering of the r pressure of the solution and hence to the lowering of the ing-point and to the rise in the boiling-point. If these are rmal, as they are, for salts, the osmotic pressure must be rmal also.

ie osmotic pressures of concentrated solutions are by no is small and pressures up to 36 atmospheres have been ured. Such a pressure is equal to that exerted by a column ater 1,200 ft. in height. And this enormous pressure it be remembered, is produced simply by the water's passing igh a semipermeable membrane into a solution without the n of any external force.

any of the processes which take place in the living organisms t least partially osmotic in their nature, the movement of sap lants and of the bodily fluids in animals, for example.

alytical Properties of Copper.—In analysis, use is most iently made of the following properties: namely, the le is but slightly soluble in water and cold dilute acids, soluble in hot dilute nitric acid (separation from mercury); sulfate is soluble in water (separation from lead); the hyide is soluble in an excess of ammonia (separation from uth); and the sulfide is soluble in potassium cyanide (separan from cadmium). The intense blue color of the cupric ionia ion which is formed by the addition of an excess of ionium hydroxide to the cupric salt is fairly characteristic, nickel is the only other metal which has similar properties. ry characteristic test for copper is based on the fact that llic iron will precipitate bright upon its to the product of the volts times the coulombs, it follows that the potential or electromotive force of a cell is equal to the free energy produced during 1 grm. equivalent of change divided by 96,500. Expressed in the form of an equation,

$$\text{E.m.f.} = \text{F}/96,500$$

in which e.m.f. stands for electromotive force, and F for the free energy of 1 [illegible] of chemical change. From this, it follows th[illegible] a cell is directly proportional to the decrease i[illegible] accompanying the transformation of a gram [illegible] oxidizing and reducing agents in the cell. Since [illegible] is different for different combinations, the pot[illegible]us cells are quite dissimilar. Oxidizing agents [illegible] in the order of their activity, *i.e.*, the decrease [illegible]y involved in the transformation of a gram eq[illegible] number can be assigned to each which represents the potential of an electrode in the normal ionic solution[1] of the oxidizing agent. This number may be represented by E and then, E = F′/96,500; where F′ is the free energy produced when 1 grm. equivalent of the oxidizing agent is reduced. The following table gives a short list of oxidizing agents arranged in the order of their oxidizing power, and also gives the value of E. This table is a part of what is called the potential series.

Agent	E in volts	Agent	E in volts
NO_3^-	+1.75	H^+	+0.277
Cl_2	+1.694	Pb^{++}	+0.129
O_2	+1.396	Ni^{++}	+0.049
Br_2	+1.270	Co^{++}	+0.045
Ag^+	+1.048	Tl^+	−0.045
Hg^+	+1.027	Fe^{++}	−0.063
Cu^{++}	+0.606	Cd^{++}	−0.143
		Zn^{++}	−0.493

A + sign before the value of E indicates that the electrode is itive against the solution of that oxidizing agent, and a – ı means that the electrode is negative toward the solution, the significance of a negative sign is that free energy is taken instead of being given out when the ion is changed to the al. This is the case with all the metals which are hard to ıce from their compounds.

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[1] A normal ionic solution is one which contains in a liter such a quantity of the salt that there will be 1 grm. equivalent of the ion present in the actually dissociated state. Because of the incomplete dissociation, such a solution will contain per liter more than one equivalent of the salt.

ny oxidizing agent in this list is able to form anything g below it and is formed by all that stand above. For mple, the cupric ion will oxidize anything from hydrogen to and change it from the element to the ion, while copper is lf oxidized by mercury and all that stand above to the cupric A voltaic cell then may be made up of a combination of any of these agents, and its electromotive force will be the braical difference between the value of E for the two electles. For example, a cell might be made up of a silver trode in a silver solution and a copper electrode in a copper tion, and it would have an e.m.f. of 1.048 – 0.606 = 0.442 s. The silver electrode would be positive toward the copper the latter would dissolve, while metallic silver would be osited. The electromotive force of the Daniell cell may be ulated from this table by subtracting the value of zinc, .493 from that of copper, +0.606; 0.606 – (–0.493) = 6 + 0.493 = 1.099 volts. Here in contrast to the above, the per is positive toward the zinc and is deposited while the dissolves.

he activity of an oxidizing agent depends upon the concention. The figures given above apply to normal ionic solus containing 1 grm. equivalent of "actual ion" per liter; in e dilute solutions, the electrodes are less positive if the oxidizagent is a cation. Anything which tends to reduce the contration of the copper ion for instance, will tend to bring the ential of the copper electrode nearer the zinc and reduce the ential of the copper zinc cell. The concentration of copper in lution containing an excess of ammonia is very small, and potential of a cell made up of a copper electrode in such a tion and a zinc electrode in zinc sulfate solution is much ller than that of the Daniell cell. If potassium cyanide is l instead of the ammonia, the concentration of the copper ill further reduced, so that the potential of the copper electrode is actually made smaller than that of the zinc; and in a cell made up of the two, the processes which take place in the Daniell cell are reversed, copper going into solution and the zinc being deposited.

SILVER

General.—Because [illegible] nce free in nature, silver has been known and us [illegible] toric times. Its relationship to the other elements [illegible] lex as will be seen by a study of its compounds. [illegible] much like copper aside from the difference in c [illegible] it is like mercury in the mercurous, and copp [illegible] ous states in that it is monovalent and also in the s [illegible] ies of its halogen compounds. It differs radically tho [illegible] h mercury and copper in that its hydroxide is a st [illegible] hat its soluble salts of strong acids are neutral. In [illegible] es the alkali metals, and some of its salts are isomorphous with the corresponding salts of potassium. The silver ion Ag^+ is a good oxidizing agent, and the metal is obtained very easily from many of its compounds. The oxide for example, when heated, acts like mercuric oxide in that it is changed into the metal and oxygen. Scheele took advantage of this in one of his methods for the preparation of oxygen.

Occurrence.—Like copper, silver is found in nature both free and in combination. The native silver is a fairly important ore, but is practically never found pure, being alloyed with gold, copper or mercury. The most important ore is the sulfide Ag_2S called argentite or silver-glance. This is usually found in isomorphous mixture with lead sulfide. In addition there are compounds of silver sulfide and antimony or arsenic sulfides known as pyrargyrite Ag_3SbS_3, and proustite, Ag_3AsS_3.

Metallurgy.—The metallurgy of silver is complicated by the fact that it is generally associated with other metals such as copper, lead, zinc and gold which it is necessary and desirable to extract at the same time. To meet the needs of individual cases, a considerable variety of methods for extracting the silver have been devised. These may be grouped into smelting or dry processes, amalgamating and leaching or wet p
The smelting methods are usually applied to ore whic
relatively more copper or lead than silver. If they

er ores, they are worked as described under that metal, the blister copper obtained will carry practically all the · in the ore. This crude copper is then purified by electroly- ınd the silver is obtained in the anode mud. The lead are smelted as will be described under that metal, and the will contain the silver. This is called work lead or base ɔn. The silver is removed from this by what is known .e Parke's process which is as follows: Work lead is melted rge kettles and kept molten for some time to allow other ırities to be oxidized and skimmed off as "dross." Then antity of zinc equal to from 0.5 to 2.0 per cent. of the weight ıe lead is stirred into the molten mass. Zinc and lead only slightly soluble in each other, while zinc is a much ɜr solvent for silver than lead is. The zinc, therefore, as an extractive solvent, and dissolves the greater part ıe silver (see the Law of Distribution) from the lead. The r zinc alloy being much the lighter, rises to the surface, and ·eing allowed to cool, forms a solid crust while the lead is molten. This is skimmed off and freed from most of the which adheres to it, and the zinc is then distilled from the · in large graphite retorts. The silver is heated in a cupella- furnace where any lead which it retains is oxidized to rge, PbO, and absorbed in the bone ash which forms the ɔm of the furnace. The silver remains unoxidized, accom- ed by any gold that was in the original bullion. These ɜeparated by dissolving the silver in hot concentrated sul- acid; the gold is left unchanged. The silver is precipi- l from the silver sulfate solution by means of metallic copper. ıere are also electrolytic processes for getting silver and from work lead. The silver and gold are found in the .ues in the bottom of the cell.

nalgamation Process.—This depends upon the solution ɜe silver from an ore in metallic mercury, forming silver amal- . After separating this from the ore gangue, it is freed from ɜs mercury by straining through canvas or buckskin. The amalgam is then distilled in an iron retort, the mercury pass- ›ver and the silver remaining in the retort. This process is icable to ore in which the silver is either free or can be easily ced to the free state.

The Halogen Compounds of Silver.—Silver fluoride may be made by the action of hydrofluoric acid upon the oxide or carbonate. It is highly soluble in water and is deliquescent.

The chloride, bromide, and iodide of silver are very slightly soluble in water or in dilute acids, and are thrown down as curdy precipitates upon the addition of the corresponding halogen salts to a solution of a silver salt. The chloride is white and soluble to the extent of 0.002 grm. per liter of water. The bromide has a pale yellow color and is less soluble than the chloride. The iodide is distinctly yellow, and is the least soluble of the three. When exposed to the light, silver chloride and bromide darken and some free halogen is formed together with a subchloride or bromide, Ag_2Cl or Ag_2Br. Silver iodide is unchanged in the light unless an excess of $AgNO_3$ is present. These facts are important in connection with photography (p. 384).

The silver halides at ordinary or lower temperatures will combine directly with ammonia for the formation of the following compounds, $2AgCl\cdot 3NH_3$, $AgCl\cdot 3NH_3$, $AgBr\cdot NH_3$, $2AgBr\cdot 3NH_3$, $AgBr\cdot 3NH_3$, $2AgI\cdot NH_3$, $AgI\cdot NH_3$.

Silver chloride is fairly soluble in concentrated solutions of hydrochloric acid and of the easily soluble chlorides, apparently because of the formation of the ion $AgCl_3^{--}$. It is also easily soluble in ammonium hydroxide owing to the formation of the stable complex ion, $Ag(NH_3)_2^+$ called the silver ammonia ion. Silver bromide is somewhat soluble in ammonium hydroxide, but the iodide is scarcely affected. The explanation is that silver bromide because of its slight solubility gives a concentration of silver as ion in the solution which is but little higher than that of the silver ion which together with the ammonia is in equilibrium with the complex silver ammonia ion, so its concentration cannot be much reduced through the formation of this ion. Silver iodide is still less soluble, and the concentration of the silver ion in its solution is smaller than that from the silver ammonia ion.

Sodium thiosulfate interacts wit [illegible] for the formation of the complex crystalline s [illegible] When in solution, this seems to giv [illegible] The concentration of the silver as [illegible] the same as that from silver ave much effect upon the latter although it dissolves silver ide with ease.

ver Cyanide.—Soluble cyanides give with the soluble silver a precipitate of silver cyanide which is somewhat less le than the chloride. The cyanide is soluble in ammonium xide and very easily in an excess of potassium cyanide to the formation of the very stable complex silver cyano- on, $Ag(NC)_2^-$, similar to the complex cuprocyanogen ion, NC)$_2^-$. The concentration of the silver ion from this ion is ry small that silver iodide, and all of the other difficultly le salts of silver, are dissolved by potassium cyanide in s. The sulfide requires the largest excess.

utions of this potassium silver cyanide are used in silver oplating. The object to be plated is made the cathode plate of pure silver the anode.

ver Nitrate.—Silver nitrate, $AgNO_3$, is the most important f silver. It is made by the action of nitric acid upon the l;

$$3Ag + 4HNO_3 = 3AgNO_3 + NO + 2H_2O$$

ver nitrate is a white crystalline easily soluble salt, iso- hous with potassium nitrate. It melts at a temperature le over 200° and when cast in sticks is sometimes used in cine as a caustic under the name of lunar caustic. Its use as stic depends upon the property of rendering insoluble certain genous substances, called the albuminoids.

the pure state, it is not altered by light; but in the presence ducing agents, it is changed to finely divided metallic silver g a black color. This is the cause of the stains which duces on the skin. The nitrate is much used in the labora- for the detection and estimation of the halogens and is the starting-point for the preparation of most of the other salts.

ver Sulfate.—Silver sulfate may be made by the action of ntrated sulfuric acid upon the metal;

$$H_2SO_4 = Ag_2SO_4 + SO_2 + 2H_2O$$

this reaction in the "parting" of the alloys are obtained in the smelting and refining

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Silver chloride is fairly soluble in concentrated solutions of hydrochloric acid and of the easily soluble chlorides, apparently because of the formation of the ion $AgCl_3^{--}$. It is also easily soluble in ammonium hydroxide owing to the formation of the stable complex ion, $Ag(NH_3)_2^+$ called the silver ammonia ion. Silver bromide is somewhat soluble in ammonium hydroxide, but the iodide is scarcely affected. The explanation is that silver bromide because of its slight solubility gives a concentration of silver as ion in the solution which is but little higher than that of the silver ion which together with the ammonia is in equilibrium with the complex silver ammonia ion, so its concentration cannot be much reduced through the formation of this ion. Silver iodide is still less soluble, and the concentration of the silver ion in its solution is smaller than that from the silver ammonia ion.

Sodium thiosulfate interacts with silver salts for the formation of the complex crystalline salt, $2NaAgS_2O_3 \cdot Na_2S_2O_3$. When in solution, this seems to give the complex ion, $AgS_2O_3^-$. The concentration of the silver as ion from this seems to be about the same as that from silver iodide for sodium thiosulfate does not have much effect upon the latter although it dissolves silver bromide with ease.

Silver Cyanide.—Soluble cyanides give with the soluble silver salts a precipitate of silver cyanide which is somewhat less soluble than the chloride. The cyanide is soluble in ammonium hydroxide and very easily in an excess of potassium cyanide owing to the formation of the very stable complex silver cyanogen ion, $Ag(NC)_2^-$, similar to the complex cuprocyanogen ion, $Cu\ (NC)_2^-$. The concentration of the silver ion from this ion is so very small that silver iodide, and all of the other difficultly soluble salts of silver, are dissolved by potassium cyanide in excess. The sulfide requires the largest excess.

Solutions of this potassium silver cyanide are used in silver electroplating. The object to be plated is made the cathode and a plate of pure silver the anode.

Silver Nitrate.—Silver nitrate, $AgNO_3$, is the most important salt of silver. It is made by the action of nitric acid upon the metal;

$$3Ag + 4HNO_3 = 3AgNO_3 + NO + 2H_2O$$

Silver nitrate is a white crystalline easily soluble salt, isomorphous with potassium nitrate. It melts at a temperature a little over 200° and when cast in sticks is sometimes used in medicine as a caustic under the name of lunar caustic. Its use as a caustic depends upon the property of rendering insoluble certain nitrogenous substances, called the albuminoids.

In the pure state, it is not altered by light; but in the presence of reducing agents, it is changed to finely divided metallic silver having a black color. This is the cause of the stains which it produces on the skin. The nitrate is much used in the laboratory for the detection and estimation of the halogens and is also the starting-point for the preparation of most of the other silver salts.

Silver Sulfate.—Silver sulfate may be made by the action of hot concentrated sulfuric acid upon the metal;

$$2Ag + 2H_2SO_4 = Ag_2SO_4 + SO_2 + 2H_2O$$

Advantage is taken of this reaction in the "parting" of the alloys of gold and silver which ar d in the smelting a of these metals. The silver is dissolved while the gold is not. It is moderately soluble in water and will combine with aluminum sulfate forming the alum $AgAl(SO_4)_2.12H_2O$, which is isomorphous with the corresponding potassium salt and with the whole series of alums.

Silver Sulfide.—Silver sulfide, Ag_2S, is so very slightly soluble that it is formed by the action of hydrogen sulfide upon all silver compounds except the complex potassium silver cyanide in the presence of a very large excess of potassium cyanide. It is even formed, as noted above, by the action of hydrogen sulfide or of other sulfides upon metallic silver.

Silver Carbonate.—S[illegible]te, Ag_2CO_3, is a pale yellow salt slightly soluble in wa[illegible]h it imparts a faint alkaline reaction. It resembles [illegible]rbonate in that it is more soluble in the presence of c[illegible]lioxide. The fact that the normal salt exists indicate[illegible]r hydroxide is a strong base.

Other Salts.—Silver [illegible] a[illegible] AgNCS (white), silver chromate, Ag_2CrO_4 (red), silver [illegible]ite, Ag_3AsO_3 (yellow) and silver arsenate, Ag_3AsO_4 [illegible]own) are a few of the salts which are used in analysis[illegible]

Photography.—The mo[illegible]ant of the modern photographic processes depend upon [illegible] sensitiveness of the silver halides toward light. The "dry plate" upon which the picture is originally taken consists of a plate of glass or a film of celluloid covered with a dried emulsion of silver bromide in gelatine.

When such a plate is exposed for a fraction of a second to light, no visible action takes place; but if it is then placed in a suitable reducing agent called the "developer," the portions of the silver bromide which were exposed to the light are reduced to metallic silver at a rate which is proportional to the intensity of the light and the time of exposure. The reduced silver is deposited as a black substance in the very position of the bromide from which it was obtained. The unexposed bromide will also be reduced by the developer but very much more slowly than that which has been acted upon by light. If the exposure was made in a camera, there will be developed upon the plate an image which in its light and shade effects is the reverse of the object, that is, it will be dark where the object is light. This is called the negative. After the plate is "developed," it has then to be "fixed;" that o say, the unchanged silver bromide must be removed so ; the plate may not be further acted upon by the light. This one by taking advantage of the solubility of the bromide in um thiosulfate or "hypo" as it is often called.

ust why the bromide which has been exposed to light is more ly reduced than the unexposed is not known with certainty, it may be connected with the fact that light will transform ito a subbromide as noted above.

rom the negative, "positives" or "prints" are made by allow- light to pass through the negative and strike sensitized paper :h is placed in direct contact with the gelatine film of the itive. The dark portions of the negative which corre- id to the light portions of the object protect the paper from action of light, and when the print is finished it will be light where the object was. Some printing-out papers are sen- ed with silver bromide and these require only very brief osure, but must be developed like plates. Others contain r chloride and the printing is continued until the image ainly visible upon the paper. Such prints are then "toned" reating them with a solution of sodium chloraurate, $NaAuCl_4$, um gold chloride as it is called. The silver which has been iced by the light, in turn reduces the gold to metallic gold :h in the finely divided state has a pleasing reddish tint. By acing the gold solution by potassium chlorplatinite, K_2PtCl_4, inum will be precipitated instead of gold, giving a very dark :. By whatever process made, the prints after development oning must be fixed by dissolving out the unchanged silver s with sodium thiosulfate.

lirrors.—Mirrors are now usually made by coating glass with r. This is done by the action of reducing agents such as the rates, glycerine, formaldehyde, or a reducing sugar upon noniacal solutions of silver nitrate. These mirrors are far rior to the old-fashioned ones which were backed with an lgam of tin.

nalytical Properties of Silver.—The silver ion is colorless, and is a difficultly soluble compound with the chlorine ion, a perty which is also possessed by the mercurous, cuprous, and ions. Analytically, the cuprous compounds are unimpor- :. Silver chlori soluble in hot wate tion from lead chloride; but is soluble in ammonium hydroxide, a distinction from mercurous chloride. In quantitative analysis, silver is usually weighed as the chloride, but often as the metal, which is obtained either by electrolysis or by oxidizing all the other metals, except gold and platinum, in the air at a high temperature and weighing the metallic bead which is so obtained, then dissolving out the silver with nitric acid or sulfuric acid and weighing the residue of gold and platinum. The difference in weight is the weight of the silver.

Gold has been known [illegible]toric times. From its striking appearance and its o[illegible] free in nature it must have been among the earli[illegible]als to attract the attention of men.

Gold forms a co[illegible]all number of compounds since all of its simple s[illegible] oxyacids are very unstable. In fact, gold seems to be [illegible]y incapable of existing as a simple ion although se[illegible]lex ions are known. The compounds of gold bel[illegible] series, the aurous in which the gold is monovalent and the au[illegible]ic in it is trivalent. These compounds are characterized by the great ease with which they decompose to give metallic gold. This, in general, may be brought about by comparatively feeble reducing agents or by a moderate rise in temperature. The simple aurous halogen compounds are not soluble in water and this establishes a sort of relationship with copper and silver.

Occurrence.—Gold generally occurs free in nature, its only native compounds being those with tellurium. Native gold is rarely found pure, being almost always alloyed with silver. It is carried in finely divided conditions in quartz and other rock materials and in pyrite, galena and other sulfides. It may be found in its original deposits in veins running through the main rock masses or in alluvial beds of sand or gravel formed by the breaking down of the original deposits through weathering action. Gold in deposits of the former kind is called reef gold while that of the latter kind is called placer gold.

Among the minerals containing gold and tellurium, syl[illegible]te, (AuAg)Te$_2$ and calaverite, [illegible]e mentioned. [illegible]se minerals are much less frequently found than native gold, but are of importance in some gold districts.

Metallurgy.—The processes for extraction of gold may be classified like those for silver as smelting, amalgamation, and leaching processes; but for gold there is an additional class, simple washing processes.

In the latter, gold in placer deposits of sand or gravel is concentrated by shaking up the material with water and allowing the gold to separate by its greater density from the lighter sands. These methods do not save all of the gold even when carried out under good conditions, and hence are used chiefly by prospectors, and in the opening up of new gold fields. They are greatly increased in efficiency if mercury is used to collect the concentrated gold as an amalgam and in this form they are rather widely used.

Amalgamation Processes.—Amalgamation processes for gold are very similar to those used for silver, and gold and silver are frequently recovered in the same operation. If the gold is disseminated in quartz or other massive rock the metal is recovered by crushing the ore in stamp mills and leading the crushed material over amalgamated plates, *i.e.*, copper plates coated with mercury. The gold is held by this mercury, and from time to time the gold amalgam is scraped from the plate; excess mercury is removed by filtering the amalgam through canvas or buckskin and the resulting solid amalgam is distilled to free the gold from mercury.

Smelting Processes.—Gold in copper or lead ores is concentrated during the smelting of these ores into the blister copper or the work lead. It is removed from these products, along with silver by the refining processes already described under silver and copper.

When both gold and silver are thus obtained, a separation or "parting" is necessary. A common method of doing this is to treat the gold-silver alloy with boiling concentrated sulfuric acid. Silver dissolves almost completely while gold is unaffected. The gold, after removal of silver sulfate solution, is melted, refined and cast into bars. Electrolytic processes are also used.

Leaching Processes.—The most important wet methods for gold extraction are *ation* and the *cyanide* pro

In the former, finely crushed gold ore containing the free metal is treated with a solution of chlorine in water. This dissolves gold, forming gold chloride, $AuCl_3$. From the solution gold is precipitated as the sulfide by means of hydrogen sulfide

The *cyanide* process, patented in 1890 by McArthur and Fo rest, is very widely used for the treatment of low grade ores th cannot be profitably worked by smelting. It is carried out allowing the crushed ore to remain in contact for a considera time with a very dilute solution of potassium cyanide, K The solution dissolves both gold and silver from the ore form potassium aurocyanide, $KAu(NC)_2$, and potassium argenti nide, $KAg(NC)_2$. The equations representing the reactions discussed in detail under the complex cyanides of gold (p. 3 Oxygen is essential, for the reaction.

To recover the precious metals the cyanide solution is pa through boxes containing zinc dust or turnings. Zinc diss while the gold and silver are precipitated;

$$2KAu(NC)_2 + Zn = K_2Zn(NC)_4 + 2Au$$
$$2KAg(NC)_2 + Zn = K_2Zn(NC)_4 + 2Ag$$

Enormous quantities of gold have been extracted by cyanide process from the low-grade ores of South Africa this has been an important factor in cheapening gold, and h raising the price of other things, and thus has contributed t "high cost of living."

The gold production for the United States in 1915 was 891,100 which is a little more than one-fifth of the wo production.

Physical Properties.—Gold has a high luster and a bea yellow color. It melts at 1,062° and has a density of It is exceedingly malleable and ductile and may be b out into leaves $\frac{1}{280{,}000}$ of an inch in thickness. Very divided gold usually has a purple color, although red, blu green colloidal solutions of the metal have been obtained. glass owes its color to finely divided gold, as does "pur Cassius" which appears to be minute particles of gold intim mixed with stannic oxide.

Gold is a very good conductor of heat and electricity bei ceeded by only silver and copper.

Chemical Properties.—Gold is even more resistant to chemical action than silver. It is not altered by oxygen at ordinary temperatures nor by hydrogen sulfide. It is not dissolved by any dilute acid nor by concentrated nitric or sulfuric acids, indicating that it requires a very strong oxidizing agent to cause the gold to pass into the ionic state. This is confirmed by the fact that it is dissolved by selenic acid which is a most active oxidizing agent. The metal is also dissolved by "aqua regia" a mixture of nitric and hydrochloric acids.

This mixture evolves chlorine and the gold is transformed by it into chlorauric acid, $HAuCl_4$, which gives the complex ion, $AuCl_4^-$. The chlorine, of course, cannot be a stronger oxidizing agent than the nitric acid which set it free, but it has the advantage in this case that the product of the reaction is very stable. Gold is also attacked by the fused hydroxides and nitrates of the alkali metals forming aurates. The soluble chlorine compounds of gold are easily reduced by even such feeble reducing agents as the ferrous salts or oxalic acid.

Because of its chemical resistivity, its beauty and its comparative rarity, gold has long been used for ornaments and for coinage. For such purposes, the pure metal is too soft and it is alloyed with copper or silver, usually the former. The gold coins of most countries contain 90 per cent. of gold or are 900 "fine"; those of England, however, contain 91.667 per cent. or are 916.67 fine. The composition of gold alloys is often expressed in carats, pure gold being 24 carat and 18 carat gold being $^{18}/_{24}$ gold.

The Oxides and Hydroxides.—Auric hydroxide $Au(OH)_3$, is formed when sodium hydroxide is added to an auric solution. It acts both as a weak base and as a weak acid. When the hydroxide is carefully heated, it goes over into auric oxide, Au_2O_3, which at higher temperatures decomposes into the elements.

Aurous hydroxide, AuOH, is formed by the action of dilute potassium hydroxide upon aurous chloride. When heated to 200° it is changed into the oxide, Au_2O, and this decomposes at 250°.

The Halogen Compounds of Gold.—Gold will combine directly with chlorine or bromine to form auric chloride or b $AuCl_3$, $AuBr_3$. These co [illegible] combine with hydro hydrobromic acid or with the corresponding halide salts, forming chlorauric or bromauric acids or their salts. The sodium chloraurate, $NaAuCl_4{\cdot}2H_2O$, is a common commercial salt and is used in photography as noted above in the toning of silver prints. Chlorauric acid is formed by dissolving gold in aqua regia.

When either the simple chloride or bromide or the complex acids are cautiously heated, aurous chloride or bromide is formed. At still higher temperatures, these decompose into the free halogen and the metal. They are not soluble in water, but slowly decompose in contact with it forming the auric compound and free gold. This is much like the behavior of some of the cuprous compounds. Auric iodide is decidedly unstable and passes easily into the aurous compound even at ordinary temperatures.

Sulfides.—Hydrogen sulfide precipitates a mixture of aurous sulfide, Au_2S, and auric sulfide, Au_2S_3 from auric solutions. These sulfides are soluble in the alkaline sulfides owing to the formation of the thioaurites, K_3AuS_2, and thioaurates, $KAuS_2$. In this respect gold is like antimony, arsenic, and tin.

The Complex Cyanides.—One of the most important chemical properties of gold is its ability to form complex ions with cyanogen; aurocyanogen, $Au(NC)_2^-$, and auricyanogen, $Au(NC)_4^-$, are well-known examples of such ions. They are formed by the action of an excess of sodium or potassium cyanide upon the compounds of gold. They are very stable and the solutions are utilized in gold electroplating, an anode of gold being used and the object to be plated being made the cathode.

The aurocyanides are of especial importance, because it is through their formation that a large part of the gold is extracted from its ores. This depends upon the fact that finely divided gold is dissolved by solutions of potassium or sodium cyanides when in contact with the air. The equation for the reaction is as follows:

$$4Au + 8KNC + O_2 + 2H_2O = 4KAu(NC)_2 + 4KOH$$

The reaction is really ionic so that it succeeds as well with the cheaper sodium cyanide as with the more expensive potassium salt.

Analytical Properties of Gold.—Gold may be detected by its reduction to the metallic state by ferrous salts, oxlaic acid, or stannous chloride. It is almost invariably determined by the fire assaying processes. This is often done as follows: a weighed quantity of the material containing gold is mixed with a relatively large quantity of lead and a little borax and heated in a shallow clay dish called a scorifier (Fig. 64) to a fairly high temperature in contact with the air. A part of the lead and practically all of the copper and other impurities in the gold save the silver are oxidized, and these together with the "gangue" form a sort of a glass with the borax and the lead oxide which is formed. At the close of this operation the molten mass is poured into a mold and allowed to cool. A lead button containing the gold and silver is obtained. This is then heated to a high temperature in contact with the air in a "cupel" or little cup made of bone ash, the lead oxidizes and the oxide is absorbed in the cupel. There is finally left a button of gold and silver. The silver is then removed by treating the alloy with nitric acid which does not dissolve the gold. The fire assay is a smelting process carried out on a small scale.

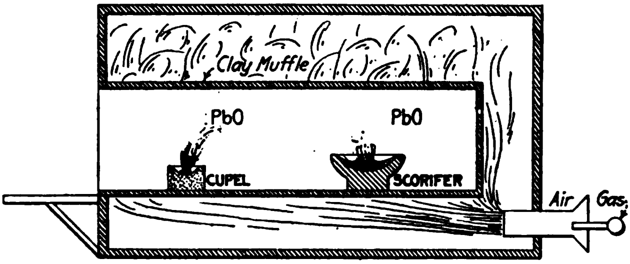

FIG. 64.

CHAPTER XXV

I

La←Y ·Ga→In→Tl

Ra m sub-group

The elements of t turally into two sub-groups, the rare earth luminum sub-group. The members of the , yttrium, and lanthanum, those of the aluminu boron, aluminum, gallium, indium, and thalli s are all trivalent although some have other tion. As was the case in groups I and II the members which stand in the left hand column of the group as it appears in the periodic system, scandium, yttrium, and lanthanum are stronger bases than those of the aluminum group which are on the right. Aluminum is the third element in the order of abundance in the earth's crust, boron is fairly abundant and all the other members of the group are decidedly rare.

The Rare Earth Metals.—The metals of the rare earths are found in a large number of rare minerals each of which contains a great many elements. The names of a few of these minerals are euxenite, gadolinite, orthite, and monazite. Monazite is found in considerable quantities in North and South Carolina, but comes chiefly from Brazil. The hydroxides of the members of this sub-group are fairly strong bases and are not soluble in excess of sodium or potassium hydroxides.

SCANDIUM

Scandium whose atomic weight is 44.1 is interesting because it is one of the elements whose existence and properties were predicted by Mendelejeff. See p. 272. Its hydroxide $Sc(OH)_3$ is a colorless gelatinous precipitate soluble in acids but not in bases. The salts are colorless and are not especially hydrolyzed. The salts of the oxy-acids as well as of the halogen acids are known.

YTTRIUM

Yttrium has an atomic weight of 89. The metal decomposes water slowly, its hydroxide is colorless and gives colorless salts. It is a stronger base than scandium hydroxide.

LANTHANUM

Lanthanum, La, atomic weight 139, is an iron-gray colored metal, which is very slowly acted upon by water. It dissolves in dilute acids. The hydroxide is white and somewhat soluble in water, the solution is alkaline, absorbs carbon dioxide and decomposes ammonium salts. It is the strongest base of the group.

There are several elements, some of them of rather doubtful individuality, whose atomic weights are near to that of lanthanum and which so far as that is concerned have a claim on the same position in the periodic system. They have so nearly the same properties that it is difficult to separate them. Ostwald has likened this group of closely related elements with about the same atomic weight which appear in the periodic system where one element might be expected, to the planetoids which are found in the solar system where one large planet might be looked for.

The Aluminum Sub-group.—The first member of Group III and of this sub-group is boron, atomic weight 11. This is almost exclusively an acid-forming element; that is to say, it does not form cations, and for that reason has already been treated among the non-metals.

ALUMINUM

General.—Aluminum is the most abundant of the metals. It is trivalent, and is like zinc in that its hydroxide is soluble both in acids and in bases. In addition to its fairly close relationship to the other members of this sub-group, it is very much like ferric iron and trivalent chromium as will be seen when these metals are studied.

Occurrence.—Aluminum is never found free but its compounds are exceedingly abundant, since it is an essential constituent of nearly all rocks except the sand-stones and limestones and is almost invariably present in these. It is found as the double silicates, the feldspars and the micas; as the simple silicate clay; as the double fluoride with sodium in cryolite; as the oxide corundum; as the hydroxide and the partially dehydrated hydroxide in [illegible] in many other compounds. The ruby is aluminu [illegible] d by a little chromium, the garnet is calcium al [illegible] e, and turquoise is a basic phosphate.

Preparation of th [illegible] lic aluminum is prepared by the electrolysis of hi [illegible] uminum oxide dissolved in a

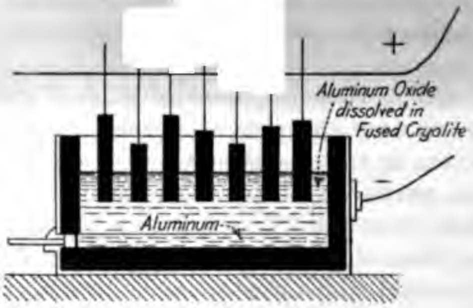

FIG. 65.

molten bath the basis of which is cryolite, Na_3AlF_6. The electrolysis is carried out in iron cells (Fig. 65) lined with carbon which is made the cathode, the anodes being large carbon rods. The current is high, about 10,000 amp. per cell, while the drop of potential around the cell is about 5 volts. The bath is kept melted by the heat produced by the current in overcoming the resistance. Upon electrolysis after the addition of the oxide, the metal collects at the cathode and runs down to the bottom of the cell while oxygen is evolved, and combines largely with the carbon anodes. As the process goes on more aluminum oxide is added from time to time, and the metal is tapped off so that the operation is continuous. This process differs materially from most metallurgical operations in that it is impracticable to purify the product, and so it is necessary to start with the very pures raw material. The aluminum oxide is made from bauxite, and the simplest process for its purification is to melt the bauxite in an electric furnace with the proper amount of carbon. This reduces the oxides of iron, silicon, and titanium which are present and leaves the aluminum oxide untouched. The metallic aluminum is very pure, often running 99.9 per cent.

Physical Properties.—Aluminum is a white metal with a bluish cast. It melts at 658° and has a density of 2.7 becoming 2.72 if it is hammered or rolled. The cast aluminum is about as hard as pure silver while the hammered is as hard as soft iron. Its tensile strength is high although much lower than that of steel. It is malleable and ductile and may be rolled or hammered into very thin sheets or drawn into fine wire. It is best worked at 100 to 150°. At temperatures near its melting-point it becomes so brittle that it may be easily powdered in a mortar. It is not readily worked in a lathe, but many of its alloys are.

Alloys with magnesium known as magnalium are very light, easily machined and fairly strong. Aluminum bronze has already been discussed under copper.

Pure aluminum has a high conductivity for electricity, about two-thirds that of copper for conductors of equal cross-section, but since the density of aluminum is so much smaller than that of copper, an aluminum conductor will weigh less than a copper conductor of equal carrying capacity.

Chemical Properties.—Metallic aluminum is really a very active element and passes into its compounds with a great decrease in free energy, and yet it acts in the main like a rather inert metal. It seems not to be acted upon by air or water or many other chemical agencies. But this indifference is apparent rather than real and is due to the formation of a very thin, closely adhering film of the oxide which acts as a sort of varnish, and in a great measure protects the metal from further attack. Aluminum may be amalgamated by contact with solutions of mercuric chloride. The aluminum oxide seems to be unable to cling to the surface of the fluid or semi-fluid aluminum amalgam, and the latter shows the real activity of the metal. It is rapidly acted upon by air and water giving hydrogen and aluminum hydroxide.

Aluminum dissolves in solutions of sodium hydroxide with the evolution of hydrogen. The explanation for this action is found in the fact that sodium hydroxide will dissolve aluminum oxide, and therefore it is supposed that it removes the protecting film from the surface of the metal and allows the latter to display its activity. Because of this protecting film, massive aluminum is but superficially attacked even at high temperatures by the air. The powdered metal, however, will burn with a very bright light when blown into a flame especially if carried by a stream of oxygen. It is sometimes used in flashlight powders. Aluminum dissolves readily in hydrochloric acid, not so easily in dilute sulfuric, and very slowly in dilute nitric. In the two former cases, hydrogen is evolved while in the latter, ammonium salts are produced. The difference in the rate of attack is probably connected with the film mentioned above. Another phenomenon which is probably due to this is, that if a piece of aluminum is made anode in certain salt solutions, sodium sulfate, carbonate, phosphate, etc., it will not allow a current to pass until a certain potential is reached, which in the case of the phosphate is 300–400 volts; while if it is made the cathode, the current passes easily at a low voltage. The aluminum electrode changes its properties very rapidly with the change in the direction of the current, and this property may be made the basis of a method for changing an alternating into a direct current. It is also of use in certain kinds of lightning arrestors.

Aluminum is trivalent in all of its compounds. Its hydroxide acts both as an acid and as a base and therefore cannot be strong in either way, consequently both classes of salts are hydrolyzed to a certain degree.

The atomic weight of aluminum is 27.1.

Goldschmidt Process.—The most striking chemical property of aluminum is its great tendency to combine with oxygen. As mentioned above this is generally concealed by the film of oxide, but under the proper conditions, aluminum will reduce all other oxides except magnesium. To bring this about, the oxide to be reduced is mixed in the proper proportions with powdered aluminum (Fig. 66) and the mixture heated at one point to a high temperature by burning magnesium or a mixture of magnesium and potassium chlorate, when a very vigorous reaction takes place which spreads through the entire mixture. The perature attained is usually high enough to melt the other al and the aluminum oxide. Naturally it varies with the le reduced. The process was invented by Goldschmidt and ed by him "Aluminothermy" and the mixtures "thermite." y are used both to get high temperatures and pure metals. equation for the reaction with ferric oxide is,

$$Fe_2O_3 + 2Al = 2Fe + Al_2O_3$$

'his reaction produces a temperature of 3,000° and is often 1 for welding operations and in the repair of breaks in large ings or forgings. It can be used almost anywhere and has ved to be of very great benefit for making repairs at a dis- ce from a machine shop. With sulfides, a very similar reac- takes place, aluminum ide, Al_2S_3, and the metal ng formed.

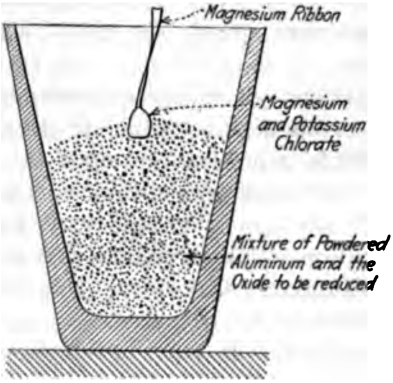
Magnesium Ribbon
Magnesium and Potassium Chlorate
Mixture of Powdered Aluminum and the Oxide to be reduced

FIG. 66.

luminum Oxide and droxide.—Aluminum le, Al_2O_3, or alumina as it often called, is found in ure in the mineral corun- a. When colored red by omium it is called ruby, n blue, sapphire. Corun- a mixed with magnetite is ed emery. Corundum is t to diamond and carborun- a (silicon carbide) in hardness, and is used for making wheels grinding. Aluminum oxide which has been fused in an elec- furnace is identical with corundum and is now being used ead of the mineral under the name "alundum." Artificial ies which are identical with the natural stones, are made by ng a mixture of aluminum oxide and a chromium compound.

luminum hydroxide is found in nature in the mineral hydrar- ite, $Al(OH)_3$, and may be made in the laboratory by the lition of a solution of a base or of a carbonate to a solution of aluminum salt. It is not soluble in 'issolved by ls and by strong bases, resembling beryllium l zinc in this respect. It differs fr in that it is very slightly soluble in ammonium hydroxide. The hydroxide dissolves in acids because of the usual dissociation of the bases into the cation and hydroxyl the concentration of the latter being decreased by the hydrogen. The bases dissolve it, because it splits off the hydrogen ion and forms the aluminate ion AlO_2^-.

$$Al(OH)_3 \rightleftarrows H^+ + H_2O + AlO_2^-$$

The hydroxyl ion of the [illegible] ites with the hydrogen ion and decreases its concentra[illegible] The salts formed are aluminates. Sodium alumi[illegible] orresponding potassium salt, $NaAlO_2$ and $KAlO_2$, [illegible] water, but are highly hydrolyzed because alumin[illegible] is a very weak acid. Most of the aluminates ar[illegible] many are found in nature; those of the bivalent meta[illegible] l spinels from the magnesium aluminate, spinel, M[illegible] is the typical mineral of the class.

Because of the great weakness of aluminum hydroxide as a base, aluminum carbonate does not exist, and aluminum hydroxide is precipitated upon the addition of carbonates to solution of aluminum salts. Obviously salts of other weak acids will work in the same way and $Al(OH)_3$ is precipitated by solutions of alkali sulfides and cyanides.

Aluminum Chloride.—Aluminum chloride, $AlCl_3$, is the most important of the artificially prepared halogen compounds of aluminum. It may be obtained in the form of a crystalline hydrate, $AlCl_3 \cdot 6H_2O$, from solutions prepared by dissolving the hydroxide or metal in hydrochloric acid. When heated to drive off the water, the chloride is completely decomposed, aluminum oxide and hydrochloric acid being formed. The anhydrous chloride may be obtained by heating the metal in chlorine or in hydrogen chloride. It is a white crystalline solid which sublimes without melting and fumes when exposed to moist air. The anhydrous salt is used in organic chemistry as a catalytic agent.

Because aluminum hydroxide is a weak base the solutions of aluminum salts, including the chloride, are acid in reaction from hydrolysis, and generally can be kept clear only in the presence of an excess of acid.

Aluminum Sulfate.—Aluminum sulfate, $Al_2(SO_4)_3 \cdot 18H_2O$, is made on a large scale from sulfuric acid and either aluminum

ide or aluminum silicate, $H_2Al_2(SiO_4)_2\cdot H_2O$ or kaolin as ten called. At the present time, the hydroxide is more nly used. It is very soluble in water and the solution because of hydrolysis. Its trade name is "concentrated It is used as a mordant in dyeing, in sizing paper ent the spreading of ink, and in clarifying water. When ion of potassium sulfate is added to a strong solution of ım sulfate, octahedral crystals of a double salt named $KAl(SO_4)_2\cdot 12H_2O$, are formed. This is the type of a large number of double salts which are isomorphous e called alums. To distinguish it from the others, it lly called potassium alum. The alums have the general ι $M^+ M^{+++} (AO_4)_2\cdot 12H_2O$ in which M^+ represents any r of the alkali metals except lithium and in addition ium, silver, and monovalent thallium; M^{+++} stands minum, gallium, indium, trivalent iron, chromium, and ıese; and finally A may be either sulfur or selenium. ıminum alums are distinguished by prefixing the name of novalent metal while in the case of the other alums both ıo- and trivalent metals are named, for example, potassium alum, $KCr(SO_4)_2\cdot 12H_2O$. The $12H_2O$ is an essential an alum. Double sulfates are known which differ from ɔnly in this respect and yet they are not alums. Since ms are isomorphous they can all form mixed crystals and crystal may contain a large number of elements.

ssium alum is the most important alum; it was formerly st important aluminum salt but has now been largely d by the sulfate. It may be prepared by roasting alunite, alum found in Italy, Hungary, and in southwestern United ınd extracting with hot water. The crystals melt or dissolve in their own water at 92°.

ions of alum are acid and will react with carbonates and nates with the evolution of carbon dioxide, the precipita- aluminum hydroxide and the formation of a solution of ates of potassium and the metal of the carbonate. It is is property that its use in cheap baking powders depends. uble sulfates formed impart a strong bitter taste to the d the use of such powders is objectionable on this account, o other. A solution of alum [illegible] olve a considerable

it is very slightly soluble in ammonium hydroxide. The hydroxide dissolves in acids because of the usual dissociation of the bases into the cation and hydroxyl the concentration of the latter being decreased by the hydrogen. The bases dissolve it, because it splits off the hydrogen ion and forms the aluminate ion AlO_2^-,

$$\mathrm{Al(OH)} \rightarrow \mathrm{H^+} + \mathrm{H_2O} + \mathrm{AlO_2^-}$$

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Because of the great weakness of aluminum hydroxide as a base, aluminum carbonate does not exist, and aluminum hydroxide is precipitated upon the addition of carbonates to solution of aluminum salts. Obviously salts of other weak acids will work in the same way and $Al(OH)_3$ is precipitated by solutions of alkali sulfides and cyanides.

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Because aluminum hydroxide is a weak base the solutions of aluminum salts, including the chloride, are acid in reactio hydrolysis, and generally can be kept clear only in the pre of an excess of acid.

Aluminum Sulfate.—Aluminum sulfate, $Al_2(SO_4)_3{\cdot}1$ made on a large scale from sulfuric acid and either an droxide or aluminum silicate, $H_2Al_2(SiO_4)_2 \cdot H_2O$ or kaolin as is often called. At the present time, the hydroxide is more mmonly used. It is very soluble in water and the solution acid because of hydrolysis. Its trade name is "concentrated m." It is used as a mordant in dyeing. in sizing paper prevent the spreading of ink, and in clarifying water. When solution of potassium sulfate is added to a strong solution of uminum sulfate, octahedral crystals of a double salt named um, $KAl(SO_4)_2 \cdot 12H_2O$, are formed. This is the type of a ther large number of double salts which are isomorphous d are called alums. To distinguish it from the others, it usually called potassium alum. The alums have the general rmula $M^+ M^{+++} (AO_4)_2 \cdot 12H_2O$ in which M^+ represents any mber of the alkali metals except lithium and in addition mmonium, silver, and monovalent thallium; M^{+++} stands r aluminum, gallium, indium, trivalent iron, chromium, and anganese; and finally A may be either sulfur or selenium. he aluminum alums are distinguished by prefixing the name of e monovalent metal while in the case of the other alums both e mono- and trivalent metals are named, for example, potassium rome alum, $KCr(SO_4)_2 \cdot 12H_2O$. The $12H_2O$ is an essential art of an alum. Double sulfates are known which differ from lums only in this respect and yet they are not alums. Since he alums are isomorphous they can all form mixed crystals and single crystal may contain a large number of elements.

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Alum loses all of its water at 100°. It is then known as burnt alum, and is us[illegible]

Mordants.—Some dyes [illegible] bine directly or enter into solid solutions with [illegible] cloth while others may be precipitated as insol[illegible] within the fiber, but many others do not have [illegible] characteristics. Such dyes require a mordant, *i.e.*, [illegible]ce which will attach itself firmly both to the fi[illegible] dye. Aluminum hydroxide is such a substance. [illegible] be dyed is first treated with a solution of an alum[illegible]uch a condition that it contains a considerable a[illegible]uminum hydroxide; neutral alum, aluminum sulfate, acetate, or sodium aluminate serve well; and it is then boiled with the dye. Dyes more often require mordants with cotton than with wool or silk. Aluminum hydroxide, even in the absence of the fiber, will take up many dyes forming what are known as "lakes."

Aluminum Acetate.—Aluminum acetate, $Al(C_2H_3O_2)_3$, may be made by the action of the sulfate in solution upon lead or barium acetate, lead or barium sulfate being precipitated. Since it is a salt of a weak acid and of a weak base it is strongly hydrolyzed, and on this account is used in mordanting cloth and also in making it waterproof. The same result may be secured at a lower cost by using aluminum sulfate and sodium acetate.

Aluminum Sulfide.—Aluminum sulfide, Al_2S_3, cannot be prepared in a wet way. It is formed by the action of finely divided aluminum on sulfides at a high temperature by practically the methods of the Goldschmidt process.

Aluminum Silicate—Clay.—The rocks which originally composed the earth's crust were very largely complex silicates and almost invariably cont[illegible]m as one of their constituents. By the action of the carbon dioxide of the air and of water, these rocks gradually decompose or weather as it is called, and aluminum silicate is one of the products. The aluminum silicate being practically insoluble and in an extremely fine state of division is carried by flowing water and deposited when the latter reaches a quiet lake or the ocean, forming the beds of clay. These evidently have a very good chance to become contaminated and are rarely pure. The purest clay, kaolin or china clay, $H_2Al_2(SiO_4)_2 \cdot H_2O$, has probably been formed by the decomposition of feldspar, $KAlSi_3O_8$, the potassium carbonate being carried away and the kaolin left where it was formed. Common clay contains some calcium carbonate, iron oxide, quartz, etc. When comparatively pure it is known as potters earth. Marl contains large quantities of calcium carbonate. Ocher, umber and sienna are clays colored by oxides of iron and manganese. They are used to some extent as pigments.

Clay, as is well known, becomes plastic when moist and may be easily worked into almost any shape desired. When dried and then heated to a high temperature it shrinks, becomes quite hard, and loses its power of becoming plastic with water. It also becomes resistant to chemical change and acquires considerable mechanical strength. Because of these properties it is used for making brick, pottery, and porcelain. The chemical change which takes place during the heating consists in the driving off of all of the hydrogen and part of the oxygen in the form of water. Pure kaolin cannot be melted in the furnaces for firing this material, but the presence of compounds of the alkalies, calcium or magnesium carbonates or especially of oxide of iron causes the mixture to fuse partially and become more or less pasty while in the furnace, and stronger after the firing. The iron imparts the red color commonly associated with brick. Fire brick is made from nearly pure clay and has a high melting-point to which it owes its name. Articles made from clay are more or less porous after firing, and for many purposes they must be glazed. This is accomplished in various ways as will develop.

Porcelain and Pottery.—Porcelain is the name applied to the highest grade of ware made from clay. It is made by grinding together very pure kaolin and feldspar in the proper proportions, and making up into a plastic mass from which the desired articles are formed. After drying, these are fired at such a temperature that the feldspar melts and binds the burned kaolin together into a hard translucent mass which is nearly homogeneous but does not have a glaze. To secure the latter the articles are dipped into a suspension of very finely ground feldspar in water, the ware becomes coated with a thin layer of the feldspar, and after drying is fired once more at a high temperature and is then allowed to cool slowly (annealed). The ware is then translucent and has a smooth glaze which is practically a glass. It is very difficultly fusible and decidedly resistant to chemical action, but is attacked by aqueous and fused alkalies.

Semiporcelain is made from a white plastic clay to which is added ground quartz, flint, or feldspar. After the first burning it is porous and is glazed with a mixture of borax, quartz, sodium carbonate, and oxide of lead. The ware is usually much thicker than porcelain and is not very suitable for chemical purposes.

Earthen-ware is made from colored plastic clay, the impurities of which serve to frit or bind the kaolin together. It is glazed by throwing common salt into the kiln toward the close of the burning. At the high temperature, the salt volatilizes and reacts with the clay and the water vapor present so as to form an easily fusible silicate which fills the pores of the ware. Unglazed earthenware is largely used in the form of tile, bricks, flower pots, etc.

Ultramarine.—A double silicate of sodium and aluminum containing some sulfur is found in nature as the mineral lapis lazuli which has approximately the composition $(NaAlSiO_4)_3 \cdot Na_2S_2$. It has a very beautiful blue color and is used for ornamental purposes. When ground it forms the pigment known as ultramarine. This same pigment may be made very cheaply by heating together sodium sulfate, carbon, and clay. The resulting blue compound is ground and washed with water. Since it is very cheap and is stable toward light, air and alkalies it is much used as a pigment in water color paints, wall paper, laundry blue, etc. It was formerly used to disguise the faint yellow color of granulated sugar. It loses its color on contact with even very weak acids and the loss of color is accompanied by the evolution of hydrogen sulfide. The blue color of the compound is something of a puzzle because its components might llly be expected to yield a colorless substance. By varying ethods of manufacture, green, violet, and red varieties may ained.

raulic Mortars and Cements.—When a limestone contain-nething like 8 to 18 per cent. of clay is "burned" in the ry way the product will slake and form a mortar which will l harden under water and hence is called hydraulic cement. h better product is made by burning a limestone which ns 20 per cent. or more of clay until the carbon dioxide is off. The substance so produced will not slake; but if ground and mixed with water, will set and harden out of t with the air. This is known as **natural cement.**

land cement is the best hydraulic cement. *It is the finely zed product made by heating to incipient fusion a properly tioned mixture of silica, aluminum silicate, and calcium ate to which an addition of not more than* 3 *per cent. of gypsum en made after the heating.* The essential constituents of nd cement are lime, silica, and alumina. Under commer-nditions some of the alumina is always replaced by ferric and a little of the lime by magnesia.

land cement may be made from almost any materials give the proper mixture of calcium carbonate, silica, and um silicate provided they do not contain more than 4 per f magnesium carbonate and that the silica is in a very fine f subdivision. The most widely used materials for the ation of this cement are limestone and clay or shale; these y finely ground and thoroughly mixed in such proportions e mixture shall contain close to 75 per cent. of calcium ate and 20 per cent. silica, alumina and ferric oxide taken er, the remaining 5 per cent. being magnesium carbonate, s, etc. Some limestones have approximately this com-n, and are called "cement rock" since they require merely dition of a little of a purer limestone or of a suitable clay ect their composition.

r the components of the cement have been ground very d thoroughly mixed in the proper proportions, they are d into the upper end of a long, slightly inclined rotary kiln h which they gradually work their way against the flames t gases of a fire of powdered coal which is blown into the metal dissolves readily in dilute and concentrated sulfuric acids and less readily in hydrochloric. Thallium forms two series of compounds. In one, the thallic series, it is trivalent and resembles aluminum to a certain degree, but the hydroxide is not soluble in bases and the sulfate does not form alums.

In the other the monovalent or thallous series it presents a curious set of rela[illegible] hydroxide, ThOH, is soluble in water and is a [illegible] The carbonate, phosphate, sulfate and oxalate a[illegible]se properties are very remarkable for a heavy m[illegible] those of an alkali metal. This resemblance is f[illegible]ed by the facts that the sulfate forms the comp[illegible]$SO_4 \cdot 6H_2O$, isomorphous with the correspondi[illegible] and also forms alums with the ferric, chromic, [illegible]lfates, which are isomorphous with ordinary [illegible]de is easily soluble while the rest of the halides a[illegible] soluble, the solubility decreasing from the chloride to the iodide. The chloride changes from white to violet in the light. The chromate is slightly soluble. In all these ways it is like silver. It resembles lead in that the chloride is not dissolved by ammonia but is by hot water.

CHAPTER XXVI

GROUP IV

Th←Ce←Zr←Ti←C→Si→Ge→Sn→Pb

members of Group IV, like those of the preceding groups, themselves into two sub-groups, which may be named anium and the germanium sub-groups. There is not as l a difference in the properties of the two as was the case ie preceding groups, and yet the same general relationship iere. The basic character of the elements increases with omic weight. The members of the titanium groups, occupy the left-hand column in the table as it is arranged, the whole, stronger bases than those on the right-hand ie germanium group. This, it will be recalled, has been e in each of the prreceding groups of metals. The gradual iing in the basic properties, which has been noticeable in ; to each successive group, is continued with this and there eally strong base formed by a member of the group, in he first two members, carbon and silicon, are distinctly etallic, and have been discussed among such elements. aximum valence of the members of the group is four.

Titanium Sub-group

members of this sub-group are titanium, atomic weight, irconium, atomic weight, 90.6; cerium, atomic weight, and thorium, atomic weight, 232.4.

Titanium

nium is a widely distributed and comparatively abundant t being present in almost all igneous rocks and forming r per cent. of the lithosphere than carbon. It does not ree in nature, and its compounds are not collected in great beds like the coal beds, so it is not as available as carbon. It occurs in a number of minerals, such as rutile, TiO_2 and titanic iron ore or ilmenite, $FeTiO_3$. The metal dissolves in acids with the evolution of hydrogen, and decomposes steam at a high temperature. It forms three series of compounds in which it is di-, tri-, and tetravalent; the last are the most stable. Titanic hydroxide is rather more of an acid than of a base but acts in both ways. Metallic titanium has a great tendency to combine with nitrogen, oxygen and sulfur. An alloy of metallic titanium with iron, called ferrotitanium, is often used in the manufacture of steel. The titanium increases the tensil strength and toughens the steel. The carbide is used in special kinds of flaming arc lamps, burning titanium carbide as cathode below a copper anode.

Zirconium

Zirconium is a rare metal, which is found chiefly as zircon, the silicate $ZrSiO_4$. Its hydroxide is a weaker acid and a stronger base than titanium hydroxide.

Cerium

Cerium is a rare metal which is chiefly found in cerite, a hydrated silicate, which contains calcium, cerium, and lanthanum, and the other rare earths which so closely resemble lanthanum. The metal burns more readily than magnesium and the small particles thrown off, when it is scratched with a hard object, take fire. For this reason an alloy of cerium and iron which gives brilliant sparks when rubbed with a file is used as a gas lighter. Cerium dioxide is used in connection with thorium dioxide in the preparation of incandescent mantles, as will soon be described. Cerium forms two series of compounds, in one it is trivalent and strongly resembles the rare earths, while in the other it is tetravalent, and is like the other titanium metals.

Thorium

Thorium is obtained chiefly from monazite, a phosphate of cerium and thorium. Thorium hydroxide is the strongest base of the titanium series. The nitrate, $Th(NO_3)_4 \cdot 6H_2O$ is the most important salt. It is used in the formation of Welsbach incandescent gas mantles. These are made by dipping a mantle woven from ramie fiber into a solution of thorium nitrate along with about 1 per cent. of cerium nitrate, $Ce(NO_3)_4$. After drying, the ramie is burned away, and the nitrates are converted into the oxides which retain the form of the mantle. A mixture of the two oxides in the proportions given is very efficient as a light producer, while pure thorium dioxide, or a mixture containing more cerium, is not nearly so good.

Thorium and its compounds are radioactive, but nowhere near as highly so as the radium compounds. A discussion of this phase of the properties of thorium will be postponed until later, when all the radioactive elements may be treated together.

GERMANIUM SUB-GROUP

The members of this sub-group are both di- and tetravalent. In their divalent compounds, they are more strongly basic than in the other series.

GERMANIUM

Germanium, atomic weight, 72.5, is a rare element. Its properties agree closely with those predicted by Mendelejeff for eka-silicon, germanium being then undiscovered. The element itself is distinctly metallic, but its compounds are much more like those of the non-metals than the metals. It bears a strong resemblance to carbon and silicon, as may be seen from the formulas of a few of its compounds, GeH_4, GeF_4, $GeCl_4$, $GeCl_2$, $GeHCl_3$ (germanium chloroform), GeO_2, GeO, GeS_2, GeS. The dioxide has acid properties, but also dissolves in acids. The sulfide, like zinc sulfide, is white.

TIN

The discovery of tin is prehistoric, the metal having been used by early man in making his bronze tools and weapons.

Occurrence and Metallurgy.—The chief ore is tin stone, or cassiterite, SnO_2. This is found in many places, but chiefly in the East Indies, Bolivia and Cornwall. It is easily reduced to the metallic state by carbon, the greatest difficulty in the metallurgy of tin being the purification of the oxide before its reduction. This is done by crushing the ore and mechanically separating the granite or other rocky gangue. The concentrated ore is then repeatedly roasted and washed to remove the sulfides of arsenic, iron and copper. The purified stannic oxide is then reduced in reverberatory furnaces with carbon in the form of anthracite coal. The [illegible] ed contains some iron and arsenic. These combine [illegible] le tin to form a compound having a higher melting-poi [illegible] e pure tin, so that the latter may be purified by care [illegible] the ingots to a very little above the melting-point [illegible] allowing the purer metal to run away from the iron ars [illegible] oy. This process is called liquation. The purest tin is [illegible] from Banca. The world's production of tin in 1914 was [illegible]) tons.

Physical Properties.—Tin [illegible] very white highly lustrous crystalline metal, which exists in several enantiotropic modifications. The one which is the most familiar is stable from 18° to 161° and is known as tetragonal, or ordinary tin. Below 18° it becomes meta-stable, and may pass over into a gray powdery modification, with a considerable increase in volume, since the density of the gray tin is 5.8, while that of the ordinary tin is 7.3. This is, of course, accompanied by the injury or destruction of any object made of the tin. The change is known as the "tin disease" and has caused the gradual decay of organ pipes, etc., in the northern part of Europe where the temperature averages lower than 18°. This change is most rapid at −50°. The transformation is very easily suspended and in the absence of the gray modification, ordinary tin will remain at temperatures somewhat below 18°, practically indefinitely. At 161°, tetragonal or ordinary tin changes into rhombic, which is stable up to the melting-point, 232°. Tin is very malleable and may be beaten or rolled into thin sheets, known as tin foil. Cast tin is crystalline and when bent gives out a peculiar sound known as the "cry of tin." Tin plate or "tin," as it is generally called, is made by dipping carefully cleaned sheets of mild steel into molten tin. The tin forms an alloy with the iron and this, in turn, becomes covered with a thin layer of practically pure tin. Such plate owes its usefulness to the fact that metallic tin is unaffected by air, water, or by weak acids in the absence of air. As is well known, very large quantities of tin plate are used in making cans and utensils. The greater part of these soon find their way to the rubbish heap and the tin is lost. This waste is regretable because the supply of tin ore seems to be limited. Attempts are being made with somewhat encouraging success to recover the metal from such waste plate. One very serious drawback is the cost of collection.

There are in use two important methods for the recovery of tin. In one the tin plate is made anode in a solution of sodium hydroxide. The tin dissolves as sodium stannate and is deposited on the cathode. In the other, the plate is exposed to the action of chlorine which attacks the tin much more easily than the iron. Each of these methods works well on the clean scrap left in the manufacture of tinned articles and about one-fourth of the tin used in this country is recovered in these ways.

A piece of tin plate which has once got a hole scratched through the tin down to the iron will rust more rapidly at that place than a piece of pure iron. This is due to the fact that in the presence of water an electric battery is formed with the iron acting like the zinc in an ordinary cell, with the result that it is rapidly corroded.

Tin is a component of many alloys; bronze has been given; soft solder contains 50 per cent. each of lead and tin; pewter, 25 per cent. lead; Britannia metal 10 per cent. antimony and some copper. Tin amalgam was formerly used to back mirrors.

Chemical Properties.—Tin forms two series of compounds, the stannous, in which it is divalent, and the stannic, in which it is tetravalent. Stannous hydroxide is more basic than stannic and its salts are less hydrolyzed in water solutions than the stannic salts, but each hydroxide is soluble both in bases and in acids and therefore each is a weak base. Neither is a strong enough base to form a carbonate. The stannous salts are good reducing agents, passing readily into the stannic compounds.

The metal is not altered by air or water at ordinary temperatures, but oxidizes easily at higher temperatures. It dissolves readily in hydrochloric acid with the evolution of hydrogen and the formation of stannous chloride, $SnCl_2$. Hot concentrated sulfuric acid forms stannous sulfate, $SnSO_4$, and sulfur dioxide.

calico printing and is called "preparing salt." It is also used to render cotton goods permanently fire proof. The cotton is first soaked in a solution of alpha sodium stannate, dried, and then placed in a solution of ammonium sulfate. In the presence of the cation of the weak base, ammonium hydroxide, the stannate is hydrolyzed and stannic acid precipitated in the cloth.

Beta or meta stannic acid is made by acting upon tin with concentrated nitric acid. [illegible] from the alpha acid in that it is entirely insoluble in nitric a [illegible] hat it swells up but does not dissolve in sulfuric acid, and [illegible] treated with hydrochloric acid forms a compound w [illegible] soluble in hydrochloric acid, but which dissolves after th [illegible] hloric acid is removed and replaced by water. The sol [illegible] obtained is not like that of stannic chloride and gelatiniz [illegible] boiled. Sodium hydroxide dissolves beta stannic acid a [illegible] a salt, sodium beta stannate, $Na_2Sn_5O_{11}4H_2O$; by acidul [illegible] solution, beta stannic acid is precipitated. When beta stannic acid is fused with sodium hydroxide, the alpha stannate is formed.

When solutions of alpha stannic acid in hydrochloric or hydrobromic acid stand for a long time, beta stannic acid is gradually precipitated.

Stannic Chloride.—Stannic chloride, $SnCl_4$, is formed by the action of chlorine upon stannous chloride or upon the metal. Use is made of this in recovering tin from scraps of the plate by the chlorine process. It is a colorless liquid, which boils at 114°. It fumes in contact with the air. With water a number of hydrates are formed. The pentahydrate, $SnCl_4{\cdot}5H_2O$, is much used in dyeing as a mordanting agent, under the name of "oxymuriate of tin." It combines with hydrogen chloride to form chlorstannic acid, H_2SnCl_6, several salts of which are known. The ammonium salt, $(NH_4)_2SnCl_6$, was formerly much used as a mordant in dyeing under the name of "pink salt," not because it had a pink color but because it was used in dyeing pinks.

Solutions of the chloride in water are very slowly hydrolyzed. The stannic hydroxide remains in solution in the colloidal st and is gradually transformed into beta stannic acid.

Stannic Sulfide.—Stannic sulfide is precipitated as amorphous substance by passing hydrogen sulfide moderately acid solution of a stannic salt. It is s trated hydrochloric acid, and is reprecipitated by diluting solution. It is also soluble in solutions of ammonium sulfide ›f the alkali sulfides, forming thiostannates,

$$SnS_2 + (NH_4)_2S = (NH_4)_2SnS_3$$

on acidulation with dilute acids, thiostannic acid is formed, ch at once decomposes to give stannic sulfide and hydrogen ide.

nalytical Properties.—The properties of stannous sulfide and se of stannic sulfide, which have just been given, put it in an lytical group with arsenic and antimony, which is dis- guished from that containing mercury, copper, cadmium, bis- th, and lead by the fact that the sulfides of the last mentioned tals are not soluble in ammonium sulfide (copper is slightly ıble). In solution, both the stannic and stannous compounds colorless. The stannous are distinguished from the stannic the dark color of the sulfide and by the fact that the former strong reducing agents.

LEAD

ead is the member of the germanium sub-group with the hest atomic weight, 207.2. Although it occurs free in nature insignificant quantities, it is so easily smelted from its ores t it was well known to the ancients. It was used by the mans for water pipes, a use to which it is still put.

he chemical relationships of lead are somewhat varied, as is en the case with the last member of a sub-group. It is both and tetravalent. In the divalent state, lead resembles ium in several ways, in others it is like silver and thallium. hydroxide, $Pb(OH)_2$, acts both as a base and an acid in that issolves and forms salts with both acids and bases. In this lead is like zinc. The hydroxide is a stronger base than acid, hat its salts with the stronger acids are fairly stable in solution. tetravalency of lead shows its relationship to the other nbers of this group, but the resemblance is not very strong. hydroxide, $Pb(OH)_4$, is both basic and acidic; but is a very k base, so that its salts, even with the strongest acid, are ctically completely hydrolyzed. The tetravalent lead com- nds tend to pass to the divalent state and are g idizing agents, so the oxidation relationships are the reverse of those between stannous and stannic tin.

Occurrence.—The principal ore of lead is galena, lead sulfide, PbS, which contains, when pure, 86.57 per cent. of lead. It is found in nearly all countries and very often carries silver, either as finely divided native silver, or as isomorphous sulfide, disseminated through it.

Other common ores e carbonate, cerusite, $PbCO_3$, and sulfate, anglesite ey are formed as decomposition or oxidation pr alena, and are consequently near the surface in mines lower down yield galena exclusively.

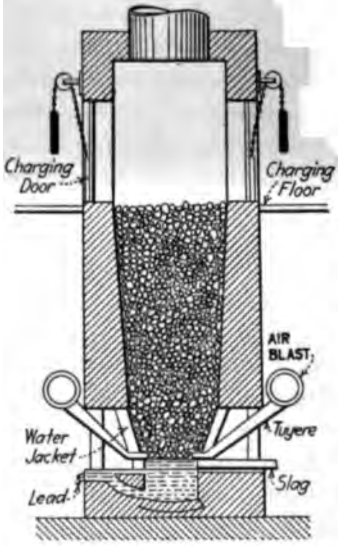

FIG. 68.

allurgy.—Since lead sulfide is ief lead ore, the extraction of om its ores is largely devoted to the treatment of this compound. This is accomplished entirely by smelting or dry processes, and the blast-furnace process is used almost exclusively.

The lead blast-furnace, Fig. 68, is rectangular in shape and is from 15 to 25 ft. high, 10 to 20 ft. long and from 3 to 5 ft. wide at the bottom. A row of blast pipes, or tuyères, along each side of the furnace, serve to introduce the air blast, which has a pressure of from 1 to 3 lb.

The lead ore mixed with coke to furnish heat for smelting, and sufficient limestones to flux off the silica from the gangue, is charged into the furnace. A part of the lead ore is charged raw, that is, unroasted, while another portion is previously roasted to lead oxide in a separate roasting furnace. This roasted ore usually has in it a considerable quantity of iron oxide, which is utilized to furnish iron for reducing lead sulfide, if not, iron oxi ore is added for this purpose.

Some of the carbon in the charge reacts with some of t oxide to form lead and carbon dio

$$2PbO + C = 2Pb + CO_2$$

Most of the remaining carbon burns to carbon monoxide which reduces the rest of the lead oxide.

$$PbO + CO = Pb + CO_2$$

and also the iron oxide

$$Fe_2O_3 + 3CO = 2Fe + 3CO_2$$

The iron formed in this way reacts with the lead sulfide of the raw ore to form metallic lead and ferrous sulfide.

$$PbS + Fe = Pb + FeS$$

Any copper in the ore is dissolved by the ferrous sulfide to form a matte which may be smelted for the copper.

The lead tapped from the blast furnace is far from pure. It is called **work lead** or **base bullion** and contains besides the gold and silver of the ore, considerable quantities of antimony, bismuth, copper, and other impurities. Most of the latter can be removed by melting the lead in large pots and keeping it molten for several hours, during which period it is frequently stirred. The impurities oxidize more readily than the lead and the oxides rise to the top as a scum or dross, which is easily skimmed off. Some lead is lost by this process, but the resulting refined product is quite soft and malleable.

This process does not remove gold and silver or all the copper. If these are in the lead, it is further treated by the Parke Process (see p. 379) to recover the gold and silver.

Not only does the lead smelting process save the gold and silver occurring in the lead ores, but it also allows the smelting of other gold and silver ores containing little or no lead, with the lead ores, to recover the precious metals and the lead.

Lead is being successfully purified on a large scale by the Betts' electrolytic process. The anodes are made of work lead, the cathodes of pure lead and the electrolyte of lead fluosilicate, $PbSiF_6$, in solution to which a little glue has been added. This latter addition has the effect that the lead is deposited in a more coherent form than in its absence. The process produces very pure lead and at the same t the precious seems to have a specific action in protecting iron from corrosi It is further used in the manufacture of glass.

Lead Dioxide.—Lead dioxide is the most stable and importa of the tetravalent compounds of lead. It is a dark brown powde which may be formed as described above, but is usually pr- pared by the action of bleaching powder upon a solution of lea plumbite,

$$Na_2PbO_2 + CaCl_2O + H_2O = PbO_2 + 2NaOH + CaCl_2$$

The dioxide is insoluble under these conditions and is precipitated. It has some tendency to act as an acid-forming oxide as is shown by the following. When fused with sodium or potassium hydroxide, it yields soluble meta-plumbates such as $K_2PbO_3 \cdot 3H_2O$, analogous to the meta-stannates. Red lead i regarded as being lead ortho-plumbate, and on this basis shoul be written Pb_2PbO_4.

Lead dioxide is a strong oxidizing agent. When heated wit hydrochloric acid, it acts like manganese dioxide and liberate chlorine, lead chloride, $PbCl_2$, being formed at the same time A few plumbic salts may be made by dissolving the dioxide i the cold concentrated acids but they all hydrolyze very easil upon dilution and reprecipitate the dioxide.

From the above it is seen that the dioxide is both basic an acidic, but is very weakly basic.

Lead Chloride.—Lead chloride, $PbCl_2$, is a white crystallin compound which is about three times as soluble in boiling wate as in water at room temperature. Advantage is taken of thi in qualitative analysis in separating lead chloride from silve and mercurous chlorides, which are but slightly soluble in eithe hot or cold water.

Lead Nitrate.—Lead nitrate, $Pb(NO_3)_2$, and acetate are almo the only lead salts of the common acids which are freely soluble water. The nitrate is made by dissolving litharge or the met in nitric acid, and crystallizing the product. It forms whi anhydrous octahedra which are isomorphous with bariu nitrate. As is to be expected from the weakness of lead h droxide, a solution of the nitrate is acid in reaction.

Lead Acetate.—Lead acetate, $Pb(C_2H_3O_2)_2 \cdot 3H_2O$, or sugar lead, is a white crystalline salt, which is easily soluble in wat e solution has a sweet taste, which gives to the salt its common ne. By boiling a solution of lead acetate with litharge a uble basic salt is formed, $Pb(OH)(C_2H_3O_2)$. This is alkaline reaction. Both the normal and the basic salts, when in ution, yield precipitates of the carbonate when acted upon carbon dioxide; the action is not complete and stops when e concentration of the acetic acid has reached a certain point. is reaction is of importance in connection with the preparan of "white lead."

Lead Carbonate and White Lead.—Normal lead carbonate, CO_3, is found in nature as the mineral cerusite and may be epared in the laboratory, but the artificial product is usually basic salt. Both the normal and basic salts are but very ightly soluble in water.

White lead is a basic carbonate which has approximately the mposition shown by the following formula, $Pb_3(OH)_2(CO_3)_2$. is much used as a pigment and is prepared in various ways. hese nearly all consist in getting the lead in solution with etic acid, and precipitating the carbonate with carbon dioxide, ereby recovering the acetic acid to be used to dissolve more lead d thus making it act as a catalyzer.

The white lead which is claimed to be the best is manufactured what is known as the old Dutch process. In principle, the ocess consists in the solution of the lead in acetic acid, with e aid of the oxygen of the air, and the precipitation of the rbonate from this by carbon dioxide, the whole process taking ace slowly at temperatures only a few degrees above that of e room. The equations are,

$$2Pb + 4HC_2H_3O_2 + O_2 = 2Pb(C_2H_3O_2)_2 + 2H_2O$$
$$b(C_2H_3O_2)_2 + 4H_2O + 2CO_2 = Pb_3(OH)_2(CO_3)_2 + 6HC_2H_3O_2$$

e lead to be "corroded" is cast into the form of perforated ks called "buckles," Fig. 69, and these are placed in the upper rt of a glazed earthenware pot, about 8 in. across. In the ttom of the pot is some crude acetic acid, and about a third of e way up, the sides of the pot are pierced by a number of holes allow circulation of air. A great number of these pots are aced side by side upon a layer of spent tan bark. They are en covered by boards and another layer of tan-bark, and upon the whole another tier of pots is placed, which are cover the same way. This is continued until a pile of many ti pots has been obtained. Bacteria grow in the tan-bark produce carbon dioxide from the oxidation of its materials the heat so generated warms the whole to a temperature able to the process. The vapors of the acetic acid, the oxy the air, and the carbon dioxide from the tan-bark being in tact with the lead bring about the reactions given above. process takes 5 or 6 weeks. At its close the heaps are taken the lead carbonate is separated from the unchanged le mechanical means and ground very fine while moist, dried then ground in linseed oil, making the pasty pigment kno white lead. Sometimes the white lead is not thoroughly

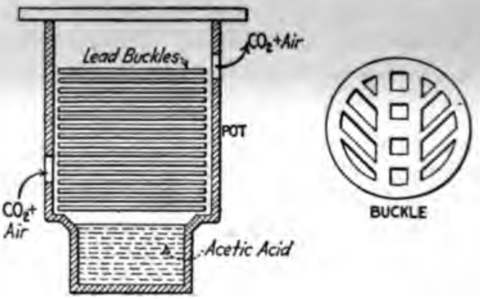

FIG. 69.

before it is ground in the oil; the result is a slightly cheape of distinctly inferior quality, which is much more rapid tacked by atmospheric agencies than that made from t carbonate.

White lead is costly, poisonous and hence dangerous to facture and use, and is so subject to atmospheric ag particularly hydrogen sulfide, that it is not suitable for cities; and yet it has held its own against other white pig which do not have these objections. The reason for this it has great covering power, *i.e.*, it is very opaque. This to the fact that the particles of white lead, although th transparent, reflect a good deal of light from each o surfaces, and any given layer of paint contains so many ov particles, each one reflecting a part of the light which pen those above that practically all of the light is turned back, and the paint is decidedly opaque.

It is a well-established fact that a cheap red barn paint will last longer than a high-priced white house paint, when both are mixed with equally good oil. The explanation offered is that the pigment in the red paint is chemically inert, while the white lead in the house paint gradually converts the oil into a more or less soluble soap which washes off. The oil used in paints must be what is known as a "drying oil" and is usually linseed oil. A "drying oil" does not evaporate as water or gasoline does, but takes up oxygen from the air and is oxidized to a tough elastic substance which binds the pigment firmly to the painted surface. "Boiled" linseed oil has been heated with lead oxide or manganous borate, these dissolve and catalyze oxidation of the oil.

Lead Chromate.—Lead chromate, $PbCrO_4$, is insoluble and is formed by bringing together in solution a soluble lead salt and a chromate. It has a fine yellow color and is used as a pigment and as a dye under the name of chrome yellow.

Lead Sulfate.—Lead sulfate, $PbSO_4$, is one of the few sulfates which are but slightly soluble. In this respect lead resembles barium. Since it is so slightly soluble, it is easily prepared by precipitation. It is less soluble in dilute sulfuric acid and in alcohol, but more soluble in dilute nitric and in concentrated sulfuric acid than in pure water. The decrease in solubility upon the addition of dilute sulfuric acid is, of course, due to the increase in the concentration of the sulfate ion. The increased solubility in concentrated sulfuric acid is probably due to the formation of the acid sulfate. The increase in solubility in nitric acid is ascribed to the fact that nitric acid is a stronger acid than sulfuric, and hence the concentration of the sulfate ion is decreased.

A basic lead sulfate $(PbSO_4)_2PbO$ known as sublimed white lead is used for a pigment. This compound is made by putting a mixture of finely powdered galena, PbS, and carbon on a brisk coke fire in a furnace. The lead sulfide is oxidized to the basic sulfate which volatilizes at the temperature of the fire, condenses in the flue and is caught in bags. It is very fine and white, and is chemically much more inert than wh

Lead Sulfide.—Lead sulfide, PbS, occurs in nature in cubical crystals, which have a gray metallic luster. It is the principal ore of lead and is called galena. In the laboratory it may be prepared as a black precipitate by passing hydrogen sulfide into an acid solution of a lead salt. It is insoluble in cold dilute acid, in sodium hydroxide or the alkali sulfides. It is soluble in concentrated hydrochloric acid, being reprecipitated upon dilution, and also in boil ic acid. In the latter case, the solution results beca idation of the sulfur ion to the element or to the

The Storage Batte battery is a voltaic cell, which, after it has w ne and produced electrical energy at the expense rgy of the reactions within the cell, may be restored to nal condition by passing a current of electricity thro ne reverse direction. It is a reversible cell. One of practical forms consists of two sets of lead plates, the one coated with lead dioxide and the other with spongy lead, the plates being placed in dilute sulfuric acid. The oxidizing agent in this case is the tetravalent lead of the lead dioxide, which gives up two positive charges to the lead electrode, upon which it is placed, and these flow through the connecting wire to the other lead electrode and there oxidize the finely divided spongy lead, which is the reducing agent, to the divalent ion. The divalent lead ion is formed at each electrode and passes into the nearly insoluble sulfate as fast as it is produced. After the cell is discharged, each electrode is coated with lead sulfate, instead of lead dioxide, or spongy lead. The cell may now be "charged" by passing a current of electricity in the reverse direction. At the anode, or dioxide plate, the divalent lead ion receives two positive charges and is changed to plumbic sulfate, which at once hydrolyzes and gives the dioxide. At the cathode, or spongy lead plate, the divalent lead ion is reduced to the metal which comes out in a spongy condition, and after somewhat more electricity has been passed through than was taken out, the cell is restored to its original condition. The excess of electricity is due to unavoidable losses. The reactions may be represented by the following equations, at the positive or dioxide plate on discharge,

$$PbO_2 + 2H_2SO_4 \rightleftarrows PbSO_4 + 2H_2O + SO_4^{--} + \otimes\ \otimes$$

vhich ⊗ ⊗ represents the two + charges given up by the avalent lead and passed through the wire to the negative or ngy lead plate, where the following reaction takes place,

$$Pb + SO_4^{--} + \otimes\ \otimes \rightleftarrows PbSO_4$$

n charging, these equations are reversed.

nalytical Properties of Lead.—Divalent lead forms a diffi- ly soluble chloride which puts it in an analytical group with er and mercurous mercury; from these it is distinguished by solubility of lead chloride in hot water. The very slight ıbility of lead sulfide in dilute acid and in alkali sulfides places ı an analytical group with mercuric mercury, copper, cadmium l bismuth. From these it is distinguished by the very slight ıbility of its sulfate, all the other sulfates of the group being ily soluble. The properties of the chromate, and hydroxide also of analytical importance.

CHAPTER XXVII

G UP V

Ta←Nd← -N→P→As→Sb→Bi
Vanad Arsenic Sub-group

The members of Gr are polyvalent elements wi
maximum valence of five group may be divided into
sub-groups, the first co of the rare and comparat
little known elemen m, columbium, neodymium
tantalum, is called n group, while the other co
ing the well-known nitrogen, phosphorus, ar
antimony, and bismuth may be called the arsenic group.
members of the arsenic sub-groups form a particularly
marked family and change their properties in a very re
manner with increasing atomic weight. The tendency
served with the preceding groups for the basicity to dec
from group to group is continued here. Nitrogen and phosp
are entirely non-metallic in their chemical and physical pr
ties; arsenic shows principally non-metallic characteristics
some few of the properties of a metal; antimony is both a
and an acid-forming element, while bismuth is almost exclu
base-forming.

Every member of Group V forms an acidic pentoxide
lower oxides are more basic, or at least less acidic in
tendencies.

VANADIUM SUB-GROUP

From the relations found in the other groups, it mig
expected that the members of this family would be more
than the corresponding ones of the arsenic group. Vana
meets this expectation for it is distinctly more basic than ar
while columbium and tantalum are apparently rat
acid than base-forming elements, but their compoun
been thoroughly studied.

These three metals all combine very vigorously with oxygen and have high melting-points.

Vanadium, atomic weight 51, forms five oxides, V_2O, VO, V_2O_3, VO_2, V_2O_5, analogous to the five oxides of nitrogen. The second and third of these are base-forming and yield the vanadous and vanadic salts, while the fourth and fifth are acid anhydrides and give the vanidites and vanidates respectively. It forms the following chlorides: VCl_2, VCl_3, VCl_4, $VOCl_2$ and $VOCl_3$. The group VO is very interesting because it acts like a complex di- and trivalent cation, forming, for example, vanadyl sulfate, $VOSO_4$, and di-vanadyl sulfate, $(VO)_2(SO_4)_3$. VO^{++} is called vanadyl and VO^{+++} di-vanadyl.

Columbium, Cb, atomic weight 93.5, and tantalum, Ta, atomic weight, 181.5, are very rare and hard to separate. Their principal compounds are the columbates and tantalates.

The atomic weight of neodymium, 144.3, seems to place this element in this group but its properties are very much like those of cerium with which it is always found associated in nature. As yet neither the element nor its compounds have found any applications.

THE ARSENIC FAMILY

The members of this family are very similar to nitrogen and especially to phosphorus; a proper grasp of their chemistry may be most readily obtained by comparison with these elements, noting the points of similarity and of difference. At the end of this chapter the whole family will be summarized in the form of a table.

ARSENIC

Occurrence.—Arsenic occurs free in nature and also in combination, chiefly in the sulfide of the metals in which it replaces a part of the sulfur, arsenical pyrite, FeAsS, may be given as an example of such a compound. It is also found as the trioxide, As_2O_3, and as the two sulfides orpiment, As_2S_3, and realgar, As_2S_2. The ores of many metals very often contain arsenic, and the removal of this element is one of the serious problems connected with

Preparation.—The element arsenic is obtained on a manufacturing scale by heating arsenical pyrite which decomposes into ferrous sulfide and arsenic,

$$4FeAsS = 4FeS + As_4$$

It may be prepared in the laboratory by reducing the trioxide with charcoal.

$$As \text{ [illegible] } + 3CO_2$$

Physical and Ch[illegible]**s.**—Arsenic forms at least three solid modific[illegible] or metallic arsenic, yellow arsenic, and a black [illegible]phous form. One of these, the ordinary or met[illegible]y much like red phosphorus, another, the yello[illegible]ly resembles yellow phosphorus. Ordinary [illegible]ay in color, very brittle and sublimes at 450° wit[illegible] Like red phosphorus, it is not dissolved by carbon disu[illegible]e, [illegible] does it phosphoresce in the air unless the temperature is raised. When heated, it burns forming As_4O_6. It is not attacked by acids with the evolution of hydrogen. Nitric acid, however, dissolves it forming oxides of nitrogen and arsenic acid, H_3AsO_4. It combines directly with the halogens, with sulfur and with many metals.

Yellow arsenic is made by rapidly cooling the vapor of ordinary arsenic. It is crystalline, sulfur-yellow in color and much more volatile than the ordinary form. Like yellow phosphorus, it is soluble in carbon disulfide and phosphoresces in the air at ordinary temperatures. It is even more poisonous than the metallic modification.

The molecular weight of the vapor of arsenic at temperatures below 600° indicates a formula of As_4 while at 1,700° it corresponds to As_2.

A black mirror-like modification of arsenic, which is deposited upon cooling the vapors under such conditions that the yellow is not formed, is considered to be another modification of arsenic, and was formerly held to be amorphous, but it has been shown to be crystalline.

Arsenic forms two series of compounds; in the one it is trivalent, and in the other pentavalent. There are a few compounds in which it is apparently divalent.

TRIVALENT COMPOUNDS

rsine.—Arsenic shows another point of similarity to nitrogen phosphorus in the formation of the hydrogen compound ne, AsH_3, analogous to ammonia and phosphine. It will be lled that ammonia has a great tendency to combine with s for the formation of ammonium salts, but that in spite of , these salts were practically completely dissociated when in form of vapor. Phosphine showed a much smaller tendency orm such salts and only a very few were stable, even in the l state. If this tendency toward instability of the salts ıld continue to increase with the atomic weight, arsine could cely be expected to form any compounds of this character, as a matter of fact none is known. Ammonia is fairly stable, is largely decomposed at higher temperatures into its eleıts; phosphine is less stable and arsine still less.

rsine may be formed by the action of water upon calcium nide, Ca_3As_2,

$$Ca_3As_2 + 6H_2O = 2AsH_3 + 3Ca(OH)_2$$

by the reduction of a soluble arsenic compound, arsenious ., H_3AsO_3 for example, by zinc or magnesium, in the presence ydrochloric or sulfuric acids,

$$H_3AsO_3 + 3Zn + 6HCl = AsH_3 + 3ZnCl_2 + 3H_2O$$

:his case, a large amount of hydrogen is given off, but the ne is easily obtained in the pure state by passing the mixture ıugh a tube surrounded by liquid air. The arsine condenses solid, melting at − 119° and boiling at − 55°, while the rogen is not liquefied at this temperature.

rsine, either pure or mixed with hydrogen, may be almost pletely decomposed into its elements by passing the gas ıugh a red hot glass tube. The arsenic is desposited beyond burner as a black mirror. Arsine kindles easily and burns ı a pale blue flame, producing water and a white smoke of nic trioxide. Within the flame itself the arsenic is evidently he free state, because if a piece of porcelain or other cold :ct be held in the flame, a mirror of arsenic will be deposited n it. The mirror of arsenic formed on the cold porcelain, or ɔsited in the glass tube beyond the burner, is so very easily seen, even when only the merest trace of a soluble compound of arsenic is introduced into the hydrogen generator, that this test, which is known as Marsh's test, is an exceedingly valuable one. Antimony behaves in much the same way, but the two mirrors may be easily distinguished as will be seen. The zinc, acid and even the glass used must be especially pure and a "blank" experiment, run without the addition of the solution suspected to contain the arsenic, to establish their st be carried out. The test is almost too delicate for or rk.

Arsine is exceedingly pois and the inhalation of even very small quantities has eath.

Arsenic Trioxide.—Arsenic e, or simply arsenic, as it is usually called, is the most imp t compound of arsenic. It occurs in nature in small qua but is generally obtained by the sublimation of the flue du smelters which roast arsenic ores.

There are two different crystalline forms of the trioxide, octahedral and monoclinic, and also an amorphous modification. In the process of purification by sublimation the arsenic trioxide collects as an amorphous glass-like substance, which, upon being kept for some time, gradually becomes milk white and looks very much like porcelain. The change in appearance is due to the passage of the amorphous into a crystalline (octahedral) modification. It is not very soluble in water, (about 2 grm. per 100 of water at 25°). As usual the amorphous is more soluble than the crystalline.

The vapor density of the trioxide at temperatures near 600° corresponds to the formula As_4O_6 and on this account it is sometimes called the hexoxide, but at 1,800° the formula indicated is As_2O_3, and this simpler one is that generally used.

The trioxide is very easily reduced by charcoal or by potassium cyanide with the formation of the metal. It acts both as an acid- and as a base-forming oxide, but is only slightly basic. With concentrated sulfuric or hydrochloric acid, it forms complicated sulfates or the trichloride, $AsCl_3$. These salts are completely hydrolyzed upon dilution with much water. The trioxide is highly poisonous, but if taken in repeated small doses, the system becomes accustomed to the substance and quantities may be taken with safety which would ordinarily be fatal.

rsenious Acid.—A solution of arsenic trioxide in water is
ntly acid, and is called arsenious acid. When attempts are
le to obtain the acid in the anhydrous state, it decomposes
water and the trioxide. The trioxide is easily soluble in
ium hydroxide solution, and from this sodium arsenite,
$_3AsO_3$, may be obtained. This sodium arsenite is an impor-
t article of commerce and is used for making sheep "dips" as
ll as for manufacturing and chemical purposes. Like all other
enic compounds, it is very poisonous. The arsenites of most
the metals, other than the alkalies are but slightly soluble.
ndon purple, impure calcium arsenite and arsenate obtained
a byproduct in the manufacture of analine dyes, and Paris
en, a copper acetate and arsenite, $Cu_2(C_2H_3O_2)(AsO_3)$, are
d as insecticides, and Scheele's green, $CuHAsO_3$, is sometimes,
ugh rarely at the present day, used as a pigment. It is
jectionable on account of its poisonous nature. Ferric hydrox-
forms very difficultly soluble arsenites, and is used as an
tidote in cases of poisoning with arsenic trioxide or its salts.
e arsenites are easily oxidized to the arsenates.

The Halogen Compounds.—Arsenic trichloride, $AsCl_3$, is the
ost important halogen compound of arsenic. It is a colorless,
y liquid, boiling at 130°. It may be formed by the action of
lorine upon arsenic, or by hydrochloric acid upon the trioxide.
hen dissolved in water, it undergoes very extensive hydrolysis
ith the formation of hydrochloric acid and arsenious acid, which
turn is largely decomposed into the slightly soluble trioxide and
ater. This action is much like that between phosphorous tri-
loride and water, with the exception that the hydrolysis of the
senic compound is reversed by the addition of concentrated
drochloric acid. Because of this, the trioxide is more soluble
hydrochloric acid than in water. Because of the volatility of
senic trichloride, precautions have to be taken before the
aporation of an acid solution of arsenic containing chlorine as
to see that the arsenic is oxidized to the pentavalent form,
d that no reduction takes place during the process. Arsenic
fluoride is a colorless liquid, while the bromide and iodide are
ids.

Arsenic Trisulfide.—Arsenic trisulfide, As_2S_3, is found in nature
the mineral called orpiment, which, upon being ground, yields

a lustrous yellow powder, which was formerly used as a pigm
It may be prepared in the laboratory by passing hydrogen su
through an acid solution of an arsenite, or of arsenious
Under these conditions, it comes down promptly as a flocc
yellow precipitate. If the hydrogen sulfide is passed throu
pure solution of arsenious acid, no precipitate will appear,
the solution beco [illegible] color, and contains the sulfi
colloidal solution in th [illegible] very small particles, as is sl
by the fact that t [illegible] y of light through the soluti
visible, and the solu [illegible] es light. The addition of
and of neutral s [illegible] he particles to gather into
and to precipitate. [illegible] g about this result, the salt
more active the higher th [illegible] ce of the cation, but the an
almost without influer

The sulfide is p [illegible] luble in even the strongest
hydrochloric acid, [illegible] s sl [illegible] vly dissolved by boiling co
trated hydrochloric acid with a volatilization of arsenic tri
ride. Strong HCl and $KClO_3$ will dissolve it with the form
of arsenic acid, H_3AsO_4, sulfuric acid and reduction produ
the chlorate. It is soluble in the alkali sulfides, giving
arsenites $(NH_4)_3AsS_3$, if the sulfide is colorless; or thioarse
$(NH_4)_3AsS_4$, if a polysulfide is used. The equations are

$$As_2S_3 + 3(NH_4)_2S = 2(NH_4)_3AsS_3$$
$$2As_2S_3 + (NH_4)_2S_5 = 2As_2S_5 + (NH_4)_2S$$
$$As_2S_5 + 3(NH_4)_2S = 2(NH_4)_3AsS_4$$

The corresponding sulfides of sodium and potassium wi
course, give sodium or potassium thioarsenites, or thioarsen
The extra sulfur of the polysulfide is the oxidizing agent,
changes the trisulfide to the penta–, which is then dissolv
form the thioarsenate. When an acid is added to one of
solutions, thioarsenious or thioarsenic acid is formed.
of these at once decomposes evolving hydrogen sulfide
precipitating a trisulfide from the thioarsenious acid, o
pentasulfide, As_2S_5, from the thioarsenic acid. This beh
of the sulfide toward alkali sulfides is very much like that
sulfides of tin and puts arsenic and tin into the same analy
group.

Colloidal Solutions.—Colloidal solutions have been repeatedly mentioned, and in each case it has been pointed out that they are visibly heterogeneous when a powerful beam of light passing hrough them is viewed by a microscope, at right angles to the ight. The minute particles in suspension are seen as points of ight in a ceaseless dance called the Brownian movement. As was explained on p. 75, this movement is supposed to be due to the hammering of the molecules of the liquid upon the suspended solute. Every solid or non-miscible liquid when exposed to water takes on an electric charge either positive or negative depending upon which kind of ion it adsorbs in the greater amount. Most colloids become negatively charged, but the hydroxides of the metals are positive. These charges on the colloid help to hold the particles apart and to keep the solute in suspension. If in any way these charges are neutralized, the particles collect together and soon settle out as a precipitate.

Arsenic sulfide is a negatively charged colloid, and the neutral salts precipitate it because the sulfide adsorbs enough of the cation to neutralize its negative charge; and then the particles gather together like newly churned butter until they are large enough to ilter out.

It will be remembered that colloids are almost without effect upon the boiling- and freezing-point of the solvent.

PENTAVALENT COMPOUNDS

Arsenic Pentoxide and Arsenic Acid.—When arsenic or the rioxide is treated with concentrated nitric acid, a solution is obtained from which, after high concentration, a hemihydrate of orthoarsenic acid, $2H_3AsO_4 \cdot H_2O$, crystallizes. This acid is a white very soluble and deliquescent substance. Like phosphoric acid, to which it is analogous, it is tribasic and forms three series of salts. The soluble normal salts are like the corresponding phosphates in that they are largely hydrolyzed and their solutions are highly alkaline. When the orthoarsenic acid is heated, it oses water and passes into the pentoxide, As_2O_5. When orthophosphoric acid is heated, the loss of water stops with the formation of metaphosphoric acid and does not go so far as to form the pentoxide.

The orthophosphates and the orthoarsenates are isomorphous and have about the same solubilities, so that it is not altogether an easy matter to distinguish between the two groups of salts. The sharpest distinction rests upon the fact that arsenic forms a difficultly soluble sulfide with hydrogen sulfide in acid solutions, while phosphorus does not.

Sodium arsenate, Na_2HAsO_4, and the bi- or pyroarsenate, $Na_4As_2O_7$, have becom[illegible] articles of commerce, being used to prepare the le[illegible]s, $Pb_3(AsO_4)_2$ or $PbHAsO_4$ which are extensively en[illegible] sprays to protect fruit trees from the attacks of insec[illegible]

Pentasulfide.—Arse[illegible]le is a yellow powder, which may be obtained, as m[illegible]e, by acidulating a solution of a thioarsenate. It is also [illegible] by passing a rapid stream of hydrogen sulfide int[illegible] arsenic acid in concentrated hydrochloric acid. [illegible] unstable substance, readily decomposing into the trisulfide a[illegible] sulfur and having about the same solubilities as the trisulfide. In dissolving in the alkali sulfides, thioarsenates are formed whether the sulfide be colorless or yellow.

Divalent Compounds.—The best known of these compounds are the iodide, AsI_2 and the sulfide, As_2S_2. The latter occurs in nature and is known as realgar. It has a red color, melts easily, and burns to arsenic trioxide and sulfur dioxide. It may be made by heating together arsenical pyrite and pyrite,

$$2FeAsS + 2FeS_2 = 4FeS + As_2S_2$$

ANTIMONY

Occurrence.—Very small quantities of antimony are found free in nature. The principal ore is a trisulfide or stibnite, Sb_2S_3. From stibnite the metal is prepared either by fusion with metallic iron, which yields antimony and ferrous sulfide, or the ore is first roasted, forming sulfur dioxide and antimony tetroxide, Sb_2O_4; the latter is then reduced by carbon. The metal prepared by either of these processes is not pure and must be remelted with sodium sulfate and slag from previous operations and finally with potassium carbonate and slag.

erties.—When pure, antimony is a silvery white, highly lline metal, which may be easily powdered and which has ity of 6.7. It melts at 630° and boils at 1,440°. The density indicates a mixture of Sb_2 and Sb_4 in the vapor at . Besides the ordinary form which has just been briefly ed, there is a very unstable yellow modification, cording to yellow phosphorus, a more stable black form, explosive kind which is deposited by electrolysis from trated solutions of the trichloride. Antimony is a cont of several important alloys. Type metal contains two f lead and one part each of tin and antimony. Like most alloys of antimony, it expands upon solidification and makes sharp castings. Babbit metal contains 1.5 per cent. , 13 per cent. antimony, 45.5 per cent. tin and 40 per ead. It is used as an antifriction metal for the bearings hinery.

imony is stable in the air at ordinary temperatures, but when heated, forming the trioxide or tetroxide, Sb_2O_4. bines directly with the halogens and is oxidized by nitric o either the trioxide or antimonic acid, H_3SbO_4, with the tion of nitrogen peroxide. Hot concentrated sulfuric acid the sulfate $Sb_2(SO_4)_3$ and sulfur dioxide. Dilute sulfuric nd hydrochloric acid are without action upon the pure

imony forms two series of compounds; in the one it is nt, and in the other pentavalent. The trivalent are the numerous and important.

Trivalent Compounds

ine.—One strong point of resemblance between antimony e preceding members of the group is the formation of the gen compound, stibine, SbH_3. This is a colorless, gaseous nce, liquefying at − 18° and freezing at − 91.5°. It is poisonous. It is formed by the action of zinc in acid solupon a soluble antimony compound. The reaction is very r to that for the preparation of arsine. Stibine is even readily decomposed than arsine and may explode. When d through a hot tube, the decomposition goes on rapidly at 200° and the antimony is deposited as a fusible non-volatile mirror on both sides of the heated portions of the tube. The mirror of arsenic from arsine is always deposited beyond the hot part of the tube and volatilizes easily without melting.

The Trioxide and Its Acids.—The density of the vapor of antimony trioxide at 1,560° corresponds with the formula, Sb_4O_6, analogous to that [illegible] r arsenic trioxides at lower temperatures. In s [illegible] formula of the substance is usually written Sb_2 [illegible] ed the trioxide, rather than the hexoxide. It [illegible] d by acting upon antimony with nitric acid or [illegible] metal in a limited supply of air. It is a white [illegible] stance which is practically insoluble in water [illegible] r nitric acid; it is soluble in moderately dilute [illegible] tartaric acid and in concentrated sulfuric acid [illegible] of sodium or potassium hydroxide. These pro [illegible] at it is both basic and acidic, and therefore not strong in eith [illegible] ay. Both series of salts are largely hydrolyzed.

The hydroxide, $Sb(OH)_3$ is a white solid which has the same solubilities as the trioxide. When the oxide or hydroxide dissolves in sodium hydroxide, sodium meta-antimonite, $NaSbO_2$, is formed. Antimony hydroxide is soluble in potassium hydrogen tartrate $KHC_4H_4O_6$ or "cream of tartar," as it is often called, owing to the formation of the complex salt tartar emetic, or potassium antimonyl tartrate, $K(SbO)C_4H_4O_6 \cdot \frac{1}{2}H_2O$. This salt is important in medicine and also in the laboratory, since it is almost the only antimony compound which will form a clear, neutral solution. The explanation of this is found in the very small ionization of the ion, Sb^{+++} from the complex antimonyl tartrate ion, $SbOC_4H_4O_6^-$. The group SbO is called antimonyl and acts like a monovalent cation. The solubility of the trioxide in tartaric acid is due to the formation of antimonyl tartrate ion. Because of the weakness of the basic properties of the hydroxide, no carbonate is known and the chloride and sulfate are largely hydrolyzed with the precipitation of basic salts. When these basic salts are boiled with water, the hydrolysis becomes completed and the trioxide is formed.

Halogen Compounds.—The most important halogen compound is the trichloride, $SbCl_3$. This [illegible] be readily prepared by di lving the trisulfide in strong hydrochloric acid and distilling. e water passes off first and then the trichloride. It is a white lid, melting at 72.0° and boiling at 233°. With a small quan- y of water it gives a white precipitate of the oxychloride, OCl, which is sometimes called antimonyl chloride. With ore water the compound $Sb_4O_5Cl_2$ is formed, and when this is shed with hot water the oxide is left behind. Hydrochloric id will reverse this hydrolysis even more readily than that arsenic trichloride.

The trichloride is used in medicine as a caustic and technically r bronzing iron, and in dyeing as a mordant.

The trifluoride, SbF_3 forms colorless crystals, which are de- quescent and whose solution may be diluted without precipita- on, owing probably to slight ionization of the salt.

The tribromide, $SbBr_3$, and triiodide SbI_3 are formed in the ame way as the chloride. They are easily decomposed by water.

Other Salts.—The salts of the oxyacids in general are not very table and are hydrolyzed even more readily than the halogen alts. The sulfate, $Sb_2(SO_4)_3$, and the nitrate, $Sb(NO_3)_3$, may be btained in solution, but the latter will not stand dilution and oon decomposes on standing, in spite of an excess of acid.

Antimony Trisulfide.—Antimony trisulfide, Sb_2S_3 is known oth in the crystalline and amorphous state. The crystalline odification is black, melts at 450°, and has a metallic luster. t is found in nature and is known as stibnite; it may also be ormed by heating the red amorphous form to 220°. The morphous modification is precipitated when hydrogen sulfide passed into an acid solution of an antimony salt. It is orange ed in color and is soluble in concentrated hydrochloric acid, but precipitated upon dilution. A method for separating arsenic nd antimony may be founded upon the difference in the behavior f their sulfides toward hydrochloric acid. Arsenic sulfide is ompletely precipitated in very strong hydrochloric acid, while ntimony is unaffected. The solution is then filtered and diluted, hen, upon the passage of more hydrogen sulfide, antimony is uantitatively precipitated as the sulfide.

Antimony trisulfide is soluble in solutions of sodium or am- onium sulfide, or polysulfide, with the formation of thio- ntimonites with the sulfides, and thioantimonates with the polysulfides, the reactions being strictly analogous to those for the arsenic compound;

$$\begin{aligned} Sb_2S_3 + 3(NH_4)_2S &= 2(NH_4)_3SbS_3 \\ 2Sb_2S_3 + (NH_4)_2SS_4 &= 2Sb_2S_5 + (NH_4)_2S \\ Sb_2S_5 + 3(NH_4)_2S &= 2(NH_4)_3SbS_4 \end{aligned}$$

The most common thioantimonate is that known as Schlippe's salt, $Na_3SbS_4 \cdot 9H_2O$.

When the solutions of the thio salts are acidulated, thioantimonious, or thioantimonic acids are formed. These acids are unstable and promptly break down into hydrogen sulfide which escapes as a gas, a ly tri- or pentasulfides, which are reprecipitated. of the sulfide in ammonium sulfide and its reprecipit cids places antimony in the analytical group with tin a ic.

PENTAVA OMPOUNDS

The pentavalent compound formed from the trivalent by the action of oxidizing age

Antimony Pentasulfide.— thod for the formation of the pentasulfide has just been given in connection with the trisulfide. The oxidizing agent in this case is the polysulfide. The pentasulfide is a yellow-red substance which like the trisulfide is soluble in strong hydrochloric acid, the sulfides of ammonium, and of the alkalies. It is reprecipitated from the hydrochloric acid solution on dilution, and from the other solutions upon acidulation. The thioantimonates have already been mentioned in connection with the trisulfide.

Antimony Pentachloride.—Antimony pentachloride, $SbCl_5$, is a colorless liquid freezing at − 6°. It is formed when an excess of chlorine acts upon powdered antimony or by the action of chlorine upon the trichloride.

When the pentachloride is treated with a little water, various hydrates are formed, while with more water it is completely hydrolyzed, giving antimonic acid, or its anhydride, the pentoxide.

Antimonic Acids and the Pentoxide.—As was the case with phosphoric and arsenic acid, there are three antimonic acid Orthoantimonic, H_3SbO_4, pyroantimonic, $H_4Sb_2O_7$, an monic, $HSbO_3$ acids. When these acids are heated they pass into the pentoxide and water. The acids and also the pentoxide are sparingly soluble in water or acids, but dissolve in potassium hydroxide. These properties indicate that the pentoxide is a purely acid-forming oxide. Potassium metantimonate, $KSbO_3$, is formed by fusing potassium nitrate with powdered antimony. When boiled with water it forms the acid pyro salt, $K_2H_2Sb_2O_7$,

$$2KSbO_3 + H_2O = K_2H_2Sb_2O_7$$

This potassium salt is easily soluble in water, but the corresponding sodium salt requires 350 parts of water for its solution, and hence is precipitated upon the addition of a concentrated solution of the potassium salt to a strong solution of a sodium salt. This is interesting as it is one of the least soluble inorganic sodium compounds. As a test for sodium, it is far less sensitive and characteristic than the flame-test.

Antimony tetroxide, Sb_2O_4, is formed by heating the trioxide to somewhere between 400° and 775° in the air. In the absence of reducing agents it is stable up to high temperatures. It is neither an acid nor a base. One large use for the substance is in the manufacture of enamel ironware for cooking purposes. In view of the highly poisonous character of antimony compounds, this use would not seem to be wholly free from objection.

BISMUTH

General.—Bismuth is far more metallic in its character than the other members of the group. The trivalent compounds are the only stable and important ones. It does not form a compound with hydrogen. Bismuth trihydroxide, $Bi(OH)_3$ is the strongest base in the family. It does not act as an acid, and does form carbonates, nitrates, phosphates, sulfates, etc. These salts are hydrolyzed by water so the hydroxide is not a really strong base. The trisulfide does not form thio salts with the alkali sulfides.

Occurrence and Preparation.—Bismuth is found free in nature and to a smaller extent as the sulfide, Bi_2S_3, and oxide, Bi_2O_3. It is obtained from its ores by first roasting them to remove sulfur, and then heating in a crucible or reverberatory furnace, with carbon to act as a reducing agent, iron to reduce unchanged sulfide, and to combine with arsenic, and fluxing material to form an easily fusible slag.

Properties.—Bismuth is a hard, brittle, crystalline metal with a high luster and a distinct reddish tinge of color. It has a density of 9.75, melts at 268° and boils at 1,420°. Its molecular weight lies between that required for the formulas Bi and Bi_2. The atomic weight is [illegible] alloys of bismuth, lead, tin and cadmium have l[illegible] which have a melting-point below the boiling-poi[illegible]ipowitz metal containing 15 parts bismuth, 8 pa[illegible] tin, and 3 parts cadmium, melts at 60°. Higher [illegible] are used as safety plugs in steam boilers and in n[illegible]atic fire extinguishers. Bismuth alloys expand [illegible]n and make good castings. Some of them are us[illegible] metal.

The metal is but ve[illegible]d upon in the air at ordinary temperatures, but when heated it [illegible] slowly oxidized to the trioxide. It requires a fairly strong oxidizing agent to transform it into ion, so it is not dissolved by hydrochloric acid in the absence of air. It is dissolved by hot concentrated sulfuric acid with the evolution of sulfur dioxide and also in the cold by nitric acid or aqua regia. In every case, a salt of trivalent bismuth is formed.

Bismuth Trioxide.—Bismuth trioxide, Bi_2O_3, is a yellow substance and is found in nature as bismuth ocher. It is made in the laboratory by heating the hydroxide, carbonate or nitrate. The trioxide has the same solubility in acids as the hydroxide, which is given below, and forms the same salts. It is not soluble in bases. The hydroxide, $Bi(OH)_3$ is a white amorphous powder and is prepared by precipitating a bismuth salt with ammonium or sodium hydroxide. It is not soluble in excess of the base and in this way differs radically from antimony hydroxide. Acids dissolve the hydroxide with the formation of salts, such as the trichloride, $BiCl_3$, or nitrate, $Bi(NO_3)_3$. When solutions of the salts are diluted, basic salts are precipitated, such as the oxychloride, $BiOCl$. In fact, clear solutions of bismuth salts can be prepared only in the presence of an excess of acid.

Bismuth Salts.—The nitrate, $Bi(NO_3)_3 \cdot 5H_2O$, is the most important salt. It forms clear colorless crystals which are

uble in dilute nitric acid, but upon dilution the solution de-
sits the basic salt, $BiONO_3$. This is called bismuth subnitrate
d is largely used in medicine. The trichloride, $BiCl_3 \cdot H_2O$, is
orless and is soluble in dilute hydrochloric acid. It forms the
ry slightly soluble oxychloride upon dilution, which is so diffi-
ltly soluble that it is used in the identification and separation
bismuth. The bromide and iodide are much like the chloride.
general, all the bismuth salts are easily hydrolyzed forming
sic salts. This hydrolysis may be reversed by acids.

Bismuth Trisulfide.—Bismuth trisulfide, Bi_2S_3, is formed by
direct union of the elements, or by the action of hydrogen
fide upon a moderately acid solution of a bismuth salt. It is
wnish-black and is not soluble in water, cold dilute acids, the
uble sulfides, or polysulfides. It is soluble in concentrated
drochloric and hot dilute nitric acid; in the latter case the
fur is either liberated or oxidized to the sulfate. These prop-
ies place bismuth in the analytical group containing mercuric
rcury, lead, copper, and cadmium. It is distinguished from
rcury by the fact that its sulfide is soluble in hot dilute nitric
d, while that of mercury is not; from lead by the slight solu-
ity of lead sulfate in dilute sulfuric acid; and from copper and
lmium by the fact that the hydroxide of bismuth is not soluble
an excess of ammonium hydroxide, while those of the other
metals are. It is finally identified by dissolving a little of
hydroxide in a few drops of dilute hydrochloric acid and pour-
the solution into water, when a white precipitate of the
chloride will form.

ther Compounds.—Besides the trioxide, bismuth forms the
noxide, BiO, the tetroxide, Bi_2O_4, and the pentoxide, Bi_2O_5.
nonosulfide, BiS, analogous to the monoxide, is known. Bis-
th dichloride and dibromide have been prepared, but no penta-
oride or bromide.

The facts collected in the following table, show that nitro-
and bismuth differ more from the other three elements than
se do from one another, but that the elements taken as a
ole form a well-defined family with fairly regular changes in
perties as the atomic weight is increased. Some of the
re striking of these changes may be summarized as follows:
the atomic weight increases, the elements change from non-

metals to metals; the melting-point, boiling-point, and density of the element rises; the boiling-point of the hydrides (except ammonia) rises; the stability of the hydrides decreases; the basic properties of the hydrides decrease; the acid properties of the oxides decrease; the basic properties of the oxides increase.

Comparison of the Properties of the Arsenic Family of Elements

	Nitrog	[illegible]	Arsenic	Antimony	Bismuth
Atomic wt.	14.01	[illegible]	74.96	120.2	208.0
Formulas	N_2	[illegible]	As_4–As_2	Sb_4–Sb_3	Bi_2–Bi
Melting-point	− 210°	[illegible]	+ 480.0°	630°	268°
Boiling-point	− 194°	[illegible]	450°	1,440° app.	1,420° app.
Density	0.89	[illegible]	3.9–5.7	6.7	9.75
Occurrence	Fr.–Cb.	[illegible]	Fr.–Cb.	Fr.–Cb.	Fr.–Cb.
Hydrides	NH_3	[illegible]	AsH_3	SbH_3	…
B.p. of hydro com.	− 33.5°	[illegible]	− 55°	− 18°	…
Comb. with acids	Salts	Salts	…	…	…
Halides.					
	…	PI_2	AsI_2	…	$BiCl_2$
A = any	NA_3	PA_3	AsA_3	SbA_3	BiA_3
halogen	…	PA_5*	AsF_5	SbA_5†	BiF_5
Oxides.					
(ous)	N_2O^1	…	…	…	…
(ic)	NO	…	…	…	BiO
(tri)	$N_2O_3{}^1$	$P_4O_6{}^1$	$As_4O_6{}^{1,2}$	$Sb_4O_6{}^{1,2}$	$Bi_2O_3{}^2$
(tetr)	N_2O_4	P_2O_4	…	Sb_2O_4	Bi_2O_4
(pent)	$N_2O_5{}^1$	$P_2O_5{}^1$	$As_2O_5{}^1$	$Sb_2O_5{}^1$	Bi_2O_5
Acids.					
hypo-ous	$H_2N_2O_2$	H_3PO_2	…	…	…
meta-ous	HNO_2	…	$HAsO_2{}^3$	$HSbO_2$	…
ortho-ous	…	H_3PO_3	H_3AsO_3	H_3SbO_3	…
meta-ic	HNO_3	HPO_3	$HAsO_3{}^3$	$HSbO_3$	…
pyro-ic	…	$H_4P_2O_7$	$H_4As_2O_7{}^3$	$H_4Sb_2O_7$	…
ortho-ic	…	H_3PO_4	H_3AsO_4	H_3SbO_4	…
Sulfides.					
	N_4S_4	…	As_2S_2	…	Bi_2S_2
tri	…	P_2S_3	As_2S_3	Sb_2S_3	Bi_2S_3
penta	N_2S_5	P_2S_5	As_2S_5	Sb_2S_5	Bi_2S_5

* Except PI_5 which is unknown.

† Except $SbBr_5$ which is unknown. 1 = acid forming. 2 = base forming. 1, 2 = both acid and base forming. 3 = known only in salts.

CHAPTER XXVIII

GROUP VI

U ← W ← Mo ← Cr ← O → S → Se → Te

Chromium sub-group **Oxygen sub-group**

The members of Group VI fall naturally into two well-marked milies or sub-groups; the first is called the oxygen or sulfur oup and is made up of oxygen, sulfur, selenium, and tellurium. hese are non-metals, although tellurium posesses some of the aracteristics of the metals. Their melting- and boiling-points e comparatively low and rise regularly with the atomic eights. These elements all form compounds with the metals hich are closely analogous, that is to say the oxides, sulfides, lenides, and tellurides are much alike. They all form comounds with hydrogen which are readily volatilized.

The members of the chromium family are chromium, molybenum, tungsten, and uranium. These are all distinctly metallic, ave very high boiling-points, are exceedingly hard, and do not rm hydrogen compounds analogous to water, hydrogen sulfide, c. The two sub-groups then differ markedly in some respects d the points of dissimilarity are about what would be expected om what has been noticed in the other groups. The elements the chromium sub-group are more metallic than those of the lfur family, have greater densities, and higher melting-points. he members of the whole sixth group have this in common that, ith the exception of oxygen, they each have a maximum normal alence of six and form the oxide RO_3, in which R stands for any ember of the group. Sulfur forms persulfuric acid, $H_2S_2O_8$, in hich its valence appears to be seven and possibly chromium has is same valence in the very unstable perchromic acid. These eptavalent compounds are to be regarded as rather abnormal r the group. The oxide is in each case the anhydride of an acid. ut the strength of the acid decreases as the atomic weight creases until with tellurium and uranium distinctly b salt which is not very soluble in water, but is dissolved by strong acids. It is about the most stable of the chromous compounds.

Chromic Compounds.—Chromium in the chromic compounds is trivalent, and the properties of the chromic ion are very much like those of aluminum, and the trivalent iron and manganese ions. All the chromic compounds are highly colored; in solution most of them are violet and this is said to be the color of the chromic ion Cr^{+++}. Som s are green, but these have different chemical properti he violet, and apparently contain complex ions. ydroxide, $Cr(OH)_3$, is very difficultly soluble, and is d when a soluble base is added to a chromic solution.

Like aluminum hydroxide, i s a base and as an acid, and so dissociates as follows:

$$Cr^{+++} + 3OH^- \rightleftarrows \quad H^+ + CrO_2^- + H_2O$$

It is soluble both in acids and in ex ess of sodium or potassium hydroxide, forming in the first case chromic salts, and in the second chromites such as $NaCrO_2$. Upon standing or more quickly when boiled, a green partially dehydrated form of the hydroxide is deposited from the chromite solutions.

Ammonium hydroxide is too weak a base to dissolve chromium hydroxide with the formation of chromite, but it does dissolve it slightly owing to the formation of complex ammonia ions. Chromic hydroxide is a very weak base, and its salts, especially those of the weaker acids, are largely hydrolyzed, so the soluble sulfides precipitate chromic hydroxide instead of the sulfide. Carbonates usually precipitate the hydroxide, but under some conditions basic carbonates may be obtained. This action is much like that of aluminum salts.

Chromic oxide, Cr_2O_3, may be made by heating the hydroxide or ammonium dichromate $(NH_4)_2Cr_2O_7$.

$$(NH_4)_2Cr_2O_7 = Cr_2O_3 + 4H_2O + N_2$$

and also by igniting a mixture of potassium dichromate, $K_2Cr_2O_7$, and sulfur

$$K_2Cr_2O_7 + S \rightleftarrows Cr_2O_3 + K_2SO_4$$

The oxide has a fine green color and is used as a pigment.

hromic Chloride.—Anhydrous chromic chloride is made by ting the metal in a stream of chlorine. It sublimes as peach- ssom-colored scales which are so slowly soluble in water that y are apparently insoluble; but in the presence of minute ntities of a powerful reducing agent, for example, a very little omous chloride, solution begins and goes on so rapidly that temperature of the system is raised several degrees, and a ge amount of the chloride goes in solution, where it exists in the omic state. Alternate reduction to the chromous and oxida- n to the chromic suggests itself as an explanation for the ion of the reducing agent.

The solution obtained in this way is green, and upon the addi- n of silver nitrate, from one- to two-thirds only of the chlorine precipitated as silver chloride. The remainder is evidently sent in complex ions. When a dilute solution of the chloride llowed to stand for some time, it becomes violet; and then whole of the chlorine may be precipitated by silver nitrate. e violet solution is also a better conductor of electricity than green. By carefully evaporating a solution of the chloride, en crystals of a hexahydrate, $CrCl_3 \cdot 6H_2O$, may be obtained; ler other conditions, two more modifications, one blue and the er green, each containing six molecules of water, may be pre- ed. When a hexahydrate is heated, it decomposes into the le Cr_2O_3, hydrogen chloride and water.

hromic Sulfate.—The normal sulfate, $Cr_2(SO_4)_3 \cdot 15H_2O$, is let in color, and its solution contains both the chromic and ate ions; but when heated, either dry or in solution, it turns en, and under certain conditions, passes into a state in which ill give reactions for neither chromic nor sulfate ions. Upon wing the solution to stand at ordinary temperature, it slowly ses back into the violet modification. The electrical con- tivity of the violet solution is much greater than that of the en under like conditions.

Chromic sulfate combines with potassium or ammonium fate to form the corresponding alum, $KCr(SO_4)_2 \cdot 12H_2O$ $NH_4Cr(SO_4)_2 \cdot 12H_2O$.

These are violet in color and are isomorphs with ordinary m. When a solution of potassium chrome alum is boiled, turns green and will then refuse to deposit crystals cooling until it has stood for some days and changed back into the violet.

Chromic Acid and the Chromates.—Strong oxidizing agents in the presence of the alkalies or their carbonates will change the di- or trivalent chromium to hexavalent with the formation of chromates. Of these, perhaps, the potassium salt, K_2CrO_4, is the most important although the sodium salt is cheaper and very largely used. Potas[illegible] is made by heating a mixture of chrome-ironston[illegible] arbonate and limestone in contact with the air. [illegible] is

$$4Fe(CrO_2)_2 + 8K_2 \text{[illegible]} K_2CrO_4 + 8CO_2 + 2Fe_2O_3$$

The limestone is [illegible] the mixture porous and so assist the oxidatio[illegible] is extracted with water, and any calcium chro[illegible] have formed is decomposed by the addition of [illegible] ate or sulphate.

The sodium salt is prep[illegible] same way using the sodium instead of the potassium carbonate. The chromates are nearly all yellow in color and have about the same solubilities as the corresponding sulfates with which they are usually isomorphous. Lead chromate is very difficultly soluble, has a brilliant yellow color and is the pigment named chrome yellow. When attempts are made to prepare chromic acid, red crystals of chromic anhydride, CrO_3, are obtained and apparently the acid, H_2CrO_4, cannot exist in the pure state.

Dichromates.—Chromic anhydride is made by adding concentrated sulfuric acid to a solution of potassium dichromate; it crystallizes out and is washed with nitric acid. It will be recalled that sulfuric acid combined with sulfuric anhydride SO_3 to form pyrosulfuric acid, $H_2S_2O_7$, and that this acid yields a series of salts called the pyrosulfates. In much the same way, chromic anhydride will combine with chromates forming the dichromates as they are, or pyrochromates, as they might be called.

$$K_2CrO_4 + CrO_3 = K_2Cr_2O_7$$

So easily does this reaction take place and so readily is chromic anhydride formed in solution, that dichromates are made by simply acidulating solutions of the chromates. This equation may best be written ionically:

$$2CrO_4^{--} + 2H^+ + SO_4^{--} \rightleftarrows 4K^+ + Cr_2O_7^{--} + SO_4^{--} + H_2O$$

ting the ions which are unchanged

$$2CrO_4^{--} + 2H^+ \rightleftarrows Cr_2O_7^{--} + H_2O$$

ction being reversible, it will at once be seen that acids easing the concentration of the H^+ will cause it to go the right, and transform chromates into dichromates, ases which will decrease the concentration of H^+ will ichromates to change into chromates. The above equa- l also make it clear why the difficultly soluble chromates barium or lead are precipitated from their soluble salts e addition of potassium dichromate. As fast as the chro- n which always exists to a certain extent in any dichro- lution is used up, more is formed from the dichromate e latter is finally practically all used up. The dichromate range red in color while the chromate is yellow; and the of color may be used as a rough indicator of the presence r OH^-.

endency of chromic anhydride to combine with chromates xhausted with the formation of dichromate as is shown existence of such compounds as ammonium trichromate Cr_3O_{10}, and the tetrachromate $(NH_4)_2Cr_4O_{13}$.

tendency for the formation of complex compounds is iore highly developed in molybdenum and tungsten.

mates and dichromates are good oxidizing agents changing hromic compounds and giving up three positive charges in ısfer for each atomic weight of chromium.

romates in acid solution will oxidize alcohol to aldehyde; to carbon dioxide; ferrous salts to ferric; and liberate ;, bromine or iodine. In either acid or alkaline solution, ll change the sulfur ion to free sulfur.

myl Chloride.—When a mixture of a dichromate and a ; is treated with a concentrated sulfuric acid, a dark red liquid distils over which bears a striking resemblance to e. This is chromyl chloride, CrO_2Cl_2:

$$+ Na_2Cr_2O_7 + 6H_2SO_4 = 2CrO_2Cl_2 + 6NaHSO_4$$

This chromyl chloride is analogous to sulfuryl chloride and like it is decomposed by water;

$$2CrO_2Cl_2 + 3H_2O = H_2Cr_2O_7 + 4HCl$$

From this, it is seen that chromyl chloride is an acid chloride but it is interesting to note that the corresponding uranium compound, UO_2Cl_2, is a salt. This is in accord with the increase in the basic properti mic weight.

Photochemical Re gelatine or glue is treated with a compound of ium, it is rendered insoluble in hot water. Use is n tanning leather which contains a sort of gelati nates or dichromates do not act in this way, but of a dichromate and glue is exposed to the sunl mate is slowly reduced and then tans the glue. lly important photochemical processes are found f a metal plate coated with a mixture of glue and ammonium hromate is exposed under an especially prepared negative and then washed with hot water, the glue is washed away where the plate has been protected from the light, but not in the other portions. The metal plate is then treated with acids, and the parts not protected by the tanned glue are partially dissolved away. Such a plate may be inked and printed from in a regular printing press and the dark spots in the object will come dark in the print.

Perchromic Acid.—When hydrogen peroxide is added to an acid solution of dichromate, a very deep blue solution is obtained which soon evolves oxygen and turns green. The deep blue solution is supposed to contain perchromic acid which is thought to have the formula $HCrO_4$. The appearance of this blue color is a delicate test for either hydrogen peroxide or a chromate.

Analytical Reactions of Chromium.—All the compounds of chromium are strongly colored; chromous, generally blue; chromic, violet or green; chromate, yellow, and dichromate orange red. Chromous compounds are too unstable to require much attention. Chromic compounds are so much like those of aluminum that they fall into the same analytical group, and are precipitated by ammonium hydroxide in the presence of ammonium salts. Chromium is most readily distinguished from ron and aluminum by the fact that its hydroxide is oxidized to odium chromate in aqueous solution by sodium peroxide. The hromate may be recognized by its strong yellow color, by the ormation of barium or lead chromate or by the blue color obtained on the addition of hydrogen peroxide to its acid solution.

MOLYBDENUM

The rather rare element molybdenum is the second member of the chromium family. It does not occur free in nature and is found chiefly as molybdenite, the sulfide, MoS_2, and also as wulfenite or lead molybdate, $PbMoO_4$. When the sulfide is roasted in the air molybdenum trioxide, MoO_3, is formed. This may then be reduced to the metal by carbon in an electric furnace, by hydrogen at a high temperature, or by aluminum using the Goldschmidt process. It is a silvery white metal which is about as hard as iron. It resembles iron in that it can be forged when hot, takes up carbon and then can be tempered like steel. It is used in the form of ferro-molybdenum alloys in the manufacture of special alloy steels. The metal is scarcely affected by oxygen up to 600° when it forms the trioxide. It is insoluble in dilute acids, except nitric.

Molybdenum forms three oxides: the sesquioxide, Mo_2O_3; the dioxide, MoO_2; and the trioxide, MoO_3. The first two are basic. The chlorides of molybdenum are Mo_3Cl_6, $MoCl_3$, $MoCl_4$, $MoCl_5$. The trioxide is the anhydride of molybdic acid, $H_2MoO_4 \cdot H_2O$. This forms a series of molybdates which are similar to the sulfates and the chromates not only in formula but also in solubility. Perhaps the most important of these salts, besides the naturally occurring lead compound, are the sodium and ammonium molybdates, $Na_2MoO_4 \cdot 10H_2O$ and $(NH_4)_2MoO_4$. The latter is much used as a reagent. Molybdic acid and its salts have a great tendency to combine with the trioxide forming complex compounds and a very large number are known. The formula of one of the sodium salts will serve to show something of the complexity of these compounds, $Na_2Mo_{10}O_{31} \cdot 21H_2O$.

Molybdenum trioxide will combine with other acids than molybdic acid to form complex acids. For exampl a series of such compounds with phosphoric acid, a form yellow crystalline very slightly soluble salts with ammonium, potassium, rubidium and cesium in the ionic state. Because of this, when a dilute nitric acid solution of ammonium molybdate is added in excess to the solution of phosphate and the whole kept warm for some time to favor the formation of the complex phosphomolybdate ion, a yellow precipitate of ammonium phosphomolybdate, $(NH_4)_3PO_4 \cdot (MoO_3)_{11} \cdot 6H_2O$, separates.

The precipitate i [illegible] ss of phosphoric acid or in alkalies, but is not s [illegible] cids which implies that the phosphomolybdic a [illegible] acid. Arsenic acid and the arsenates react with [illegible] to form compounds which are very much lik [illegible] lybdates in appearance and solubility.

When an acid s [illegible] ybdate is acted upon by a reducing agent such [illegible] fide, sulfur dioxide or dilute stannous chloride, a [illegible] which deposits a blue precipitate is formed. The [illegible] on of the precipitate is in doubt, but by some it is regarded as the molybdate of tetravalent molybdenum, $Mo(MoO_4)_2$ or Mo_3O_8.

TUNGSTEN

Tungsten is a rather rare element which has recently become of great economic importance. It occurs principally in wolfram, an iron-manganese tungstate $(FeMn)WO_4$. In the preparation of the metal from wolfram, the ore is first heated with sodium carbonate to form sodium tungstate which is then dissolved in water. When the solution of sodium tungstate is acidulated, tungstic acid is precipitated. By gently heating the acid, it is converted into the trioxide which may be reduced to the metal in a number of ways; by carbon, hydrogen, zinc, or aluminum at rather elevated temperatures. Because of the very high melting-point of tungsten which is about 3,500°, the element is usually obtained in the form of a powder; but a homogeneous mass of the metal may be secured by reducing the oxide with aluminum, if an excess of powdered aluminum is used and the mixture is wet down with liquid air rich in oxygen before it is set off. The extra high temperature necessary for the fusion of the tungsten is furnished by the powdered aluminum burning in the oxygen f the liquid air. The almost instantaneous change of tempera-ure in this case from $-182.5°$ to over 3,500° is, to say the least, triking. The metal is darker colored than zinc, is crystalline, arder than glass, very brittle, and has a density of 19.6. One f the modern applications of tungsten is in the construction of igh efficiency incandescent electric lamps, a use for which its very high melting-point renders it well adapted. The preparation of very fine wires required for such filaments is a matter of some difficulty, but it has been successfully done by compressing the powdered metal into rods and then rolling and drawing these down while they are heated by an electric current in an atmosphere of hydrogen. Lamps prepared from this tungsten are very durable and because of their high efficiency have almost replaced the old carbon lamps. The old style standard 16-cp. carbon lamp consumed about 60 watts. The corresponding tungsten lamp uses 25 watts and gives about 20 cp., so the tungsten lamp gives one-fourth more light on less than half the energy which means that it converts the electrical energy more efficiently into light and produces less heat. It is estimated that the replacement of the carbon lamps by tungstens has made a saving of several hundred millions of dollars per year in the country's light bill. A still further improvement has been made by filling the lamps with nitrogen or still better, argon. In these 0.5 of a watt or even a little less will give 1 candlepower.

Another important application of tungsten is in the preparation of special steels such as "high-speed steel." For this purpose a ferrotungsten is often prepared in the electric furnace. High-speed steel through increasing the rate at which machines and machinists can work, has lowered the cost of automobiles on an average of $200 per machine and made a corresponding saving in other lines. Hence tungsten is economically very important.

The metal is fairly resistant to chemical action, but when powdered it will burn at a red heat to the trioxide. The ordinary acids act upon it very slowly; aqua regia dissolves it readily. It reacts with chlorine to form the hexachloride, WCl_6, from which the chlorides WCl_2, WCl_4, and WCl_5, may be obtained by reduction. In addition to the trioxide already mentioned, a dioxide, WO_2, is known. The sodium tungstate, $Na_2WO_4 \cdot 2H_2O$, is used as a mordant and for rendering cotton fabric fireproof, for which purpose it is dissolved in the starch with which the articles are treated. Very complex tungstic acids and the tungstates are formed by the union of the trioxide in varying quantities with the acid or the tungstates. Compounds very similar to the phosphomolybdates are formed by the interaction of tungstic acid with phosphoric and other acids which makes the chemistry of tungsten ve

The atomic weigh 184.0.

Uranium, which is nt of the chromium family, has the highest ato .2, of any known element. It occurs in a numb minerals, but is chiefly obtained from pitchble ins the oxide, U_3O_8, or carnotite which is a va um and potassium. These ores are interesting as furnishing principal source of radium compounds. The metal may be prepared from the tetrachloride by reduction with metallic sodium, or from the oxide by reduction with carbon or aluminum. Pure uranium is much like iron. It has a white color, takes a high polish, has a density of 18.7, and melts at about 1,500°. The powdered metal is rather easily attacked chemically. It is oxidized in the air and burns in oxygen and the halogens at moderately elevated temperatures. There are two well-known oxides of uranium, the dioxide, UO_2, and trioxide, UO_3. When treated with acids, the dioxide gives a series of salts called uranous salts such as uranous chloride, UCl_4, uranous sulfate, $U(SO_4)_2 \cdot 8H_2O$, etc. The trioxide is both basic and acidic. With acids it forms a series of salts called uranyl salts. These contain the group $UO_2{}^{++}$ which acts like a complex divalent cation. These salts have a yellow color and many of them have a greenish-yellow fluorescence. The most important of the uranyl salts and in fact the most important of the uranium compounds is uranyl nitrate, $UO_2(NO_3)_2 \cdot 6H_2O$. The addition of a soluble hydroxide to a uranyl salt produces a precipitate of a diuranate, analogous to the dichromates. The sodium salt, $Na_2U_2O_7$, is difficultly soluble and has a fine yellow color. It is an article erce under the name uranium yellow and is used to color ranium glass which, like many other uranium preparations, has a reenish-yellow fluorescence. This phenomenon is due to the bsorption of the invisible ultra-violet rays of the sunlight by he uranium compound and their conversion into visible greenish ays. Any substance which is able to become luminous, while nder the excitation of some form of energy, without becoming heated to incandescence is said to be fluorescent. Fluorescence was first observed in connection with fluorspar and from this, received its name. Fluorescence differs from phosphorescence in that the former exists during the continuance of an exciting cause while the latter persists after its removal.

Metallic uranium and all of its compounds are radioactive and in fact the phenomena of radioactivity were first discovered by Becquerel in 1898 in the uranium compounds. The radioactivity of these substances is far less than that of the radium compounds and is about the same as that of the thorium salts. Again we shall have to postpone a full discussion of the subject to a later point.

CHAPTER XXIX

GROUP VII

$Mn \leftarrow F \rightarrow Cl \rightarrow Br \rightarrow I$

Manganese Halogen sub-group

With the exception of fluorine, which forms no oxy-compounds, the members of the halogen family show a variety of valencies from one up to seven. Each member of the family forms a compound with hydrogen in which the halogen is monovalent. They are typical non-metallic elements.

Manganese is the only member of the family which occupies the left-hand column of Group VII in the periodic system. It continues the regularities which have been noticed in the preceding groups in that it is much more basic than the right-hand family; it is unmistakably a metal. It does not form a compound with hydrogen analogous to the hydrohalogen acids nor is it monovalent in any compound. The strongest resemblance between manganese and the halogens is found in the heptoxide, Mn_2O_7, and the corresponding permanganic acid, $HMnO_4$. These are analogous to chlorine heptoxide, Cl_2O_7, and perchloric acid, in fact potassium permanganate, $KMnO_4$, is isomorphous with potassium perchlorate, $KClO_4$.

Manganese has a rather large number of valencies. It is di-, tri-, tetra-, hexa-, and heptavalent and with each alteration of valence it changes it chemical relationships, and points of similarity to additional elements become prominent. This makes the chemistry of manganese somewhat complicated. It will be seen in what follows that in the divalent form it is closely related to magnesium; in the trivalent state to chromium and iron; in the tetravalent condition to tetravalent lead and tin; while the hexavalent manganese is like sulfur in the sulfates and the heptavalent resembles chlorine in the perchlorates.

Occurrence.—Manganese is a fairly abundant and widely distributed element. Reference to the table on p. 274 will show that it stands between barium and strontium in its abundance.

t is found chiefly in the form of the dioxide, pyrolusite, MnO_2, o which frequent reference has been made in the past since it is much used substance. Other less abundant ores are braunite, Mn_2O_3, manganite, $Mn_2O_3 \cdot H_2O$, hausmanite, Mn_3O_4, manganese lende, MnS, and manganese spar, $MnCO_3$. The metal is obained by the reduction of its oxides with carbon in an electric urnace or more readily by their reduction with aluminum by the Goldschmidt process. Alloys of manganese with iron containing rom 10 per cent. to 90 per cent. of manganese may be prepared n blast furnaces or in electric furnaces. Those containing up o 20 per cent. are called spiegeleisen while from 20 per cent. to 90 per cent. they are known as ferromanganese. These alloys re much used in the manufacture of steel. One alloy of manganese and copper containing about 30 per cent. manganese is known as manganese bronze. It possesses great tensile strength and is very hard.

Properties.—Pure manganese is a reddish-gray metal which is very brittle and is so hard that it will scratch glass. Its melting-point is 1,260°. It is readily volatilized in the electric furnace. It holds its luter in the air but is easily dissolved by acids, even by acetic, with the evolution of hydrogen and the formation of the divalent or manganous salts. When heated to a little over 1,200° in a stream of nitrogen it takes fire and burns, forming a nitride. In this respect it is much like magnesium.

Divalent or Manganous Compounds.—The manganous salts are very much like the salts of magnesium. In many cases the two series have about the same solubility and are isomorphous. The manganous salts may be prepared by dissolving the metal, the carbonate, or any of the oxides in the acid of the salt desired and heating. The manganous salts are the only ones which are stable in acid solutions and all the others pass into them. Nearly all of them have a delicate pink color which is much more pronounced in the crystals than in the solutions. The hydroxide, $Mn(OH)_2$, is thrown down as a white precipitate when a soluble hydroxide is added to a manganous salt solution. It has about the same solubility and strength as a base as the corresponding magnesium hydroxide, and like the latter, it is soluble in ammonium salts because of the decrease in the concentration of the hydroxyl through the formati n hydroxide. This solution quickly darkens because of the oxidation of the manganous ion to the manganic, Mn^{+++}, by the oxygen of the air and the precipitation of manganic hydroxide, $Mn(OH)_3$, which is too weak a base to be dissolved by ammonium salts since it is even weaker than aluminum hydroxide. Manganous oxide may be prepared by gently heating the hydroxide in the absence of air Manganous carbonate, $MnCO_3$, is formed as a white precipitat [illegible] ble carbonate is added to a manganous salt sol [illegible] in nature where it is often found in isomorpho [illegible] magnesium carbonate. The precipitated carbona [illegible] ium carbonate, is soluble in ammonium salts a s [illegible], ammonium hydroxide and carbonic acid being [illegible] case.

Manganous sulfate [illegible] lly crystallizes with $4H_2O$, but below 6° it has 7H [illegible] orphous with ferrous sulfate, while from 7° to 20°, [illegible] contains $5H_2O$, and is isomorphous with copper sulfa [illegible] rms the double salt, $K_2SO_4 \cdot MnSO_4 \cdot 6H_2O$, with potassium sulfate which is isomorphous with the corresponding salt of magnesium and in fact with the whole series of these double salts.

Manganous sulfide, MnS, is the most soluble of the sulfides of the heavy metals. Its solubility product is so great that it cannot be precipitated by hydrogen sulfide except in the presence of hydroxyl or a very large amount of an acetate such as sodium acetate. It is usually precipitated by ammonium sulfide and generally comes down as an amorphous flesh colored substance which is readily soluble in all acids, but it sometimes appears as a green powder. When exposed to the air, the sulfide oxidizes rapidly and passes back into solution as the sulfate.

Manganous Ammonium Phosphate, $MnNH_4PO_4$, is formed under similar conditions to those for the formation of magnesium ammonium phosphate, and has closely the solubility and appearance of the latter so that it is not difficult to confuse the two.

Manganous Borate, $MnH_4(BO_3)_2$, is a salt which is of technical importance because it acts as a catalytic agent in the drying of oils and varnishes.

Trivalent Manganese.—The trivalent compounds of manganese or the manganic compounds as they are usually call not as numerous nor as stable as the manganous. A s he chloride may be obtained by dissolving manganic hydroxide, $Mn(OH)_3$, is cold hydrochloric acid, but it soon evolves chlorine and passes into manganous chloride. The sulfate, $Mn_2(SO_4)_3$, s a violet-red powder which is very deliquescent and hydrolyzes with extreme ease with the precipitation of the hydroxide. It forms alums with rubidium and cesium sulfates. A few slightly dissociated salts, such as the fluoride, MnF_3, and the phosphate, $MnPO_4$, have been prepared which are not hydrolyzed. These salts give reddish-violet solutions. Manganese sequioxide, Mn_2O_3, which is the oxide corresponding to the manganic salts occurs in nature as the mineral braunite.

Tetravalent Manganese.—Manganese dioxide is the principal tetravalent compound of manganese and is, in fact, the most important compound of the element. Like lead dioxide which it resembles in a number of ways, it is both feebly basic and acidic. When treated with cold hydrochloric acid it is dissolved to form the tetrachloride, $MnCl_4$,

$$MnO_2 + 4HCl = MnCl_4 + 2H_2O$$

This hydrolyzes upon dilution with the precipitation of the dioxide. When heated, the tetrachloride decomposes into the dichloride and chlorine,

$$MnCl_4 = MnCl_2 + Cl_2$$

It was with the aid of these reactions that the chlorine of the world was formerly prepared, and large quantities are still made in this way although the processes involving the electrolysis of the chlorides have largely replaced it. The tetrahydroxide, $Mn(OH)_4$, may be prepared by the action of powerful oxidizing agents upon manganous salts in neutral or alkaline solutions. In acid solutions the manganese compounds all tend to pass into the divalent state, while in alkaline solutions they tend to become tetravalent and to be precipitated as the dioxide or its hydroxide. This hydroxide is a weak acid and forms salts called the manganites of which calcium manganite, $CaMn_2O_5$, may be taken as an example.

Like lead dioxide, manganese dioxide is a conductor of electricity and is used as an oxidizing agent in the ordinary form of salammoniac battery known as the Leclanché cell as well as in the slightly modified type called the dry cell. In each of these, the oxidizing agent is the dioxide and the reducing agent is metallic zinc. The dioxide is reduced to the manganous ion and the zinc oxidized to the zinc ion. The electrolyte is ammonium chloride solution containing some zinc chloride. The manganese dioxide is very slightly soluble, so it is necessary to have a very large area for the positive electrode which is of carbon packed around with the dioxide. Because of the slight solubility of the dioxide, the cell "polarizes" rapidly owing to the exhaustion of the dioxide which is in solution and in contact with the carbon electrode. It is then necessary to let the cell stand until more of the dioxide is dissolved. For this reason, the cell must be used on an open circuit. Some idea of the magnitude of the dry cell industry may be obtained from the fact that about 50,000,000 of these cells are made in this country per year.

Hexavalent Manganese, The Manganates.—By fusing manganese dioxide or, in fact, almost any manganese compound with potassium hydroxide in contact with the air, or more rapidly by the addition of a nitrate or chlorate, a dark green mass containing potassium manganate, K_2MnO_4, is formed;

$$2MnO_2 + 4KOH + O_2 = 2K_2MnO_4 + 2H_2O$$

This is soluble in water giving a green solution from which crystals may be obtained which are isomorphous with potassium sulfate. Sodium manganate crystallizes from solution with ten molecules of water, $Na_2MnO_4 \cdot 10H_2O$, and is isomorphous with the decahydrate of sodium sulfate. From these two examples, it will be seen that the manganates are analogous to the sulfates, and consequently hexavalent manganese to hexavalent sulfur. Solutions of manganates have an exceedingly intense green color, but are stable only in the presence of a hydroxide. Manganic acid cannot be prepared because it at once decomposes into permanganic acid and the dioxide, but its anhydride, MnO_3, has been obtained as a reddish deliquescent powder which is very unstable.

Heptavalent Manganese, The Permanganates.—When a solution of a manganate is diluted or acidulated, the color changes through blue and violet to purple and at the same time manganese dioxide is precipitated. The change is due to the oxidaın of a portion of the manganate to the permanganate at the pense of the remainder which is reduced to the dioxide,

$$3K_2MnO_4 + 2H_2O = 2KMnO_4 + 4KOH + MnO_2$$

ıis reaction can be easily understood if the equation be written the ionic form omitting the ions which do not enter directly to the reaction,

$$3MnO_4^{--} + 2H^+ = 2MnO_4^- + 2OH^- + MnO_2$$

ıce H^+ is consumed in the reaction and OH^- produced, this ıction will take place much more readily when the solution is dulated. Even a very weak acid will bring about this change, a solution of a manganate gradually becomes purple upon posure to the air from the absorption of carbon dioxide and e formation of carbonic acid.

The transformation of the manganate into the permanganate oxidation and may be brought about by passing chlorine into e solution of the manganate. In this case, the chlorine is luced to the ion Cl^- and the whole of the manganate is oxised to the permanganate so that manganese dioxide is not ecipitated,

$$2K_2MnO_4 + Cl_2 = 2KMnO_4 + 2KCl$$

In the permanganate ion MnO_4^-, since each oxygen carries o negative charges, see p. 184, the manganese must have seven sitive charges while in the manganate, MnO_4^{--}, on the same sis the manganese carries six, and in the dioxide, MnO_2, four sitive charges. Then when one gram ion of the manganate is luced to the dioxide the manganese gives up two + charges in ssing from + 6 to + 4 and these two + charges are just fficient to raise the manganese in two gram ions of the mannate from + 6 to + 7 or in other words, to oxidize them to the rmanganate. Reference to the equations given above will ow that this is the case, and three gram moles of manganate eld two gram moles of permanganate to one of manganese oxide. Each atomic weight of chlorine gives up a + charge passing into the chlorine ion Cl^-, and hence a mole of chlorine n oxidize two moles of manganate.

The permanganates are powerful oxidising agent [illegible] infectants and are manufactured in large quantities for such purposes. The sodium salt is the cheapest if a pure article is not demanded. It is so very soluble that it is not easily obtained pure. For laboratory purposes the potassium salt is generally used. This crystallizes well in purple crystals with a greenish luster, and is isomorphous with potassium perchlorate.

Solutions of potassium permanganate of known concentration are much used in the laboratory in the volumetric determination of easily oxidizable substances such as ferrous iron, oxalic acid or manganous salts, since the permanganate acts in a rapid and definite manner with these substances. In carrying out the operation, the permanganate solution is added from a burette to the solution to be tested and the volume necessary to give to the latter the purple color of the permanganate is noted. The operation is especially convenient since, owing to the strong color of the permanganate, no other indicator is necessary. When the permanganate is used in this way, it is reduced to the manganous ion in acid solutions or to manganese dioxide in neutral or alkaline solutions. The titration of ferrous iron or oxalic acid is carried out in acid solutions, so the manganese in passing from the heptavalent to the divalent state gives up five + charges, and hence one mole of permanganate is able to oxidize five moles of a reducing agent which takes up one + charge per mole, or two moles of the permanganate can oxidize five moles of reducing agent which takes up two + charges as is the case with the oxalate ion.

The following equations represent the reaction mentioned above,

$$5Fe^{++} + MnO_4^{-} + 8H^{+} = 5Fe^{+++} + Mn^{++} + 4H_2O$$

or

$$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O$$

$$5C_2O_4^{--} + 2MnO_4^{-} + 16H^{+} = 10CO_2 + 2Mn^{++} + 8H_2O$$

or

$$5H_2C_2O_4 + 2KMnO_4 + 6HCl = 10CO_2 + 2KCl + 2MnCl_2 + 8H_2O$$

As has been mentioned, the permanganate is reduced to manganese dioxide in neutral or alkaline solutions, and also in these same solutions, the manganous ion tends to oxidize to the tetravalent condition and to be precipitated as the dioxide. The result of these tendencies is that manganous compounds may be titrated by permanganate in neutral solutions. In going from the permanganate to the dioxide, the manganese gives up three + charges, and the manganous in going to the dioxide takes up two + charges; hence two moles of permanganate will oxidize three moles of manganous salt as shown in the following equation,

$$2KMnO_4 + 3MnSO_4 + 2H_2O = K_2SO_4 + 2H_2SO_4 + 5MnO_2$$

The solution tends to become acid which would interfere with the reaction, so the titration is carried on in the presence of an excess of zinc oxide which neutralizes the acid as it is formed. The behavior of permanganate as an oxidizing agent can be readily kept in mind by remembering that in acid solutions it gives up five plus charges and goes to the manganous state, while in neutral or alkaline solutions it gives up three charges and becomes manganese dioxide.

When dry potassium permanganate is heated to 240° it decomposes into oxygen the manganate and manganese dioxide,

$$2KMnO_4 = O_2 + K_2MnO_4 + MnO_2$$

This gives purer oxygen than the decomposition of the chlorate which generally yields some chlorine.

A solution of permanganic acid may be prepared by the second general method for the preparation of acids, using barium permanganate and sulfuric acid. It has the deep purple color of the permanganates and decomposes upon boiling or exposure to the light. An impure solution of the acid is also formed whenever a manganese compound is boiled with moderately dilute sulfuric or nitric acid and red lead or lead dioxide. The equation in the latter case is,

$$2MnSO_4 + 5PbO_2 + 3H_2SO_4 = 2HMnO_4 + 5PbSO_4 + 2H_2O$$

Because of the strong and very characteristic color of the permanganate ion, this constitutes one of the best tests for manganese. It is necessary, however, to have the solution highly acid and to use a very small quantity of manganese as otherwise the action stops with the formation of the dioxide. Manganese heptoxide, Mn_2O_7, is formed by dissolving potassium permanganate in cooled concentrated sulfuric acid and carefully adding water when the oxide separates as a dark reddish-brown liquid which decomposes with the evolution of oxygen and explodes at the slightest provocation.

Analytical Properties of Manganese.—The solubility of manganese sulfide in acids and its precipitation by ammonium sulfide puts this element in an analytical group with zinc, cobalt, and nickel. From these it is distinguished by the pink color of its sulfide, by the formation of permanganic acid as described just above, by the green mass of manganate which is formed by fusion with an alkali and a nitrate, or by the amethyst color which all manganese compounds give in a borax bead heated in the oxidizing flame.

CHAPTER XXX

GROUP VIII

Fe —Co —Ni
Ru—Rh—Pd
Os —Ir —Pt

An examination of Group VIII of the periodic system will how that it differs radically from the other groups in that it is nade up of three families of closely related metals in which he similar elements occur side by side, and have about the same tomic weight, instead of forming a perpendicular column ith widely different atomic weights. There is, however, some milarity in the perpendicular columns, particularly between e last two families.

The three sub-families of the group are:

The iron sub-group: iron, atomic weight 55.84, cobalt, atomic eight, 58.97, and nickel, atomic weight, 58.68.

The ruthenium sub-group: ruthenium, atomic weight 101.7, odium, atomic weight 102.9, and palladium, atomic weight 06.7.

The platinum sub-group: osmium, atomic weight 190.9, iridm, atomic weight 193.1, and platinum, atomic weight 195.2.

All the members of the group are true metals and are somehat remarkable for the number of complex compounds which hey form.

From the gradual increase in the maximum valence which as been observed in the preceding groups, it might be anticiated that the valence of the members of this group would reach ght. The only known compounds of this kind are the tetxides of ruthenium and osmium, RuO_4 and OsO_4 and osmium ctofluoride, OsF_8.

THE IRON FAMILY

Iron forms three series of compounds: the ferrates in which is hexavalent anganese, and chrom n the

general, the more stable. Nickel forms only one s
the nickelous, but shows some tendencies toward h
in the oxide, Ni_2O_3. The members of this family
netic, have high melting-points and decompose ste
temperature.

IRON

General.—This is truly the age of iron, as may
the fact that the United States alone produces yea
000,000 long tons of the metal. A moment's thou
that our present civilization would be very differ
not have iron and steel in such abundance. I
known and used from prehistoric times. Many
composed chiefly of metallic iron, and the earliest i
weapons were probably made from this source.
iron are easily reduced by carbon, and even v
peoples have known how to do this in a small
production on anything like the modern scale h
possible since the invention of the blast furnace.

Occurrence.—Native iron is found in meteorites,
deposits in Greenland; but all that is used is o
compounds. The principal ores are hematite,
Fe_2O_3; brown iron ore or hydrated ferric oxide,
this is also called brown hematite, bog ore or limoni
magnetic iron oxide, Fe_3O_4; and siderite, spathic i

brought into a suitable mechanical state; at the same
the sulfur content is reduced to a point where it is no longer
ctionable. This makes what was a waste product, a valuable
ce of iron. More than 50,000,000 tons of iron ore are mined
year in this country, the greater part of this comes from a
on around the south and west of Lake Superior. It is mined
reat open pits with steam shovels, loaded directly into cars
taken to the harbors on the lake, transferred to ships and
ied to the lower lakes, where it is either unloaded and smelted
the spot, or taken by train to the great iron smelters around
tsburg which are conveniently located with respect to the
l fields and manufacturing centers. Within recent times a
nber of mammoth iron and steel plants have been located on
shores of the Great Lakes, so it looks as though Pittsburg
y lose its pre-eminence in this industry. Another important
1-producing region is around Birmingham, Alabama, which
near at hand both iron ore and coal. Everything must be
le as cheaply as possible because the average price of pig iron
normal times is about $15 per long ton.

Metallurgy of Iron.—The manufacture of all forms of iron and
el begins with the making of cast iron in a blast furnace.
is depends for its usefulness upon the fact that by properly
ecting and proportioning the materials put into the furnace,
impurities in the ore and the products of the reactions may
be removed as gases or liquids, and the operation made con-
ious for a long time. The materials used are coke, iron ore,
l limestone. The coke burns and gives the necessary high
perature, and also furnishes the requisite reducing agent,
bon monoxide. The limestone is changed to lime which
cts with the silicious impurities in the ore to form an easily
ble slag, consisting of calcium and aluminum silicates, which
emoved from the bottom of the furnace in the liquid state.
modern blast furnace is a very large affair; 80 to 100 ft. in
ght by about 22 ft. in greatest diameter. Its shape is approxi-
tely that of two truncated cones set base to base. It is made
steel plates and lined with very infusible silicious fire brick.
diagrammatic sketch of a blast furnace is shown in Fig. 70.
limestone, ore and coke in the proper p charged
t the top. A h ry air is bl to 16

plant, thus freezing out the water. This helps, because the water vapor in the air would react with the coke with the formation of carbon monoxide and hydrogen and the absorption of much heat. The saving in fuel caused by drying amounts to 20 per cent. and the output of the blast furnace is increased by the same amount.

The cast iron as it comes from the blast furnace is impure and contains from 4 to 11 per cent. of foreign substances, chiefly carbon, silicon, manganese, sulfur and phosphorus. These substances lower the melting-point of the iron and make it crystalline and brittle over all ranges of temperature. Cast iron, therefore, is not suitable for any purpose which requires considerable tensile strength, but may be used for castings which will be subjected to compression without much impact. There are two varieties of cast iron—white and gray. The white kind is made by rapid cooling; it contains the carbon in chemical combination and is very hard and brittle. The gray iron is made by slow cooling. It is tougher and softer than the white and contains a large part of the carbon in the form of crystals of graphite scattered through the mass.

By removing these impurities more or less completely, the iron may be converted into steel or wrought iron and thereby acquires much more valuable properties. More than three-quarters of the pig iron manufactured is subjected to such purification processes. *The first step in each of these is to take advantage of the fact that the impurities mentioned are more easily oxidized than the iron, and hence will be eliminated before the latter is attacked in case the crude substance is exposed to oxidation.* This oxidation is done either by the oxygen of the air or by that from iron oxide. It is difficult to draw the line between wrought iron and steel because the division is arbitrary, but the following is in common usage. Wrought iron is slag-bearing, contains less than 0.12 per cent. carbon, and does not harden materially when suddenly cooled. It is made in puddling furnaces. Steel is iron which is malleable at least over some range of temperature, contains from 0.12 to 2.2 per cent. of carbon, and which when suddenly cooled, is materially hardened. It is made in Bessemer converters, open hearth furnaces, or in crucibles.

Bessemer Process.—Kelly, an American, invented and patented in 1852 the process of purifying molten pig iron by blowing air through it. Bessemer, an Englishman, patented in 1855 the converter or vessel best adapted to carry out the process. After litigation, the Kelly interests sold out to the Bessemer, and the process now bears the name of the latter.

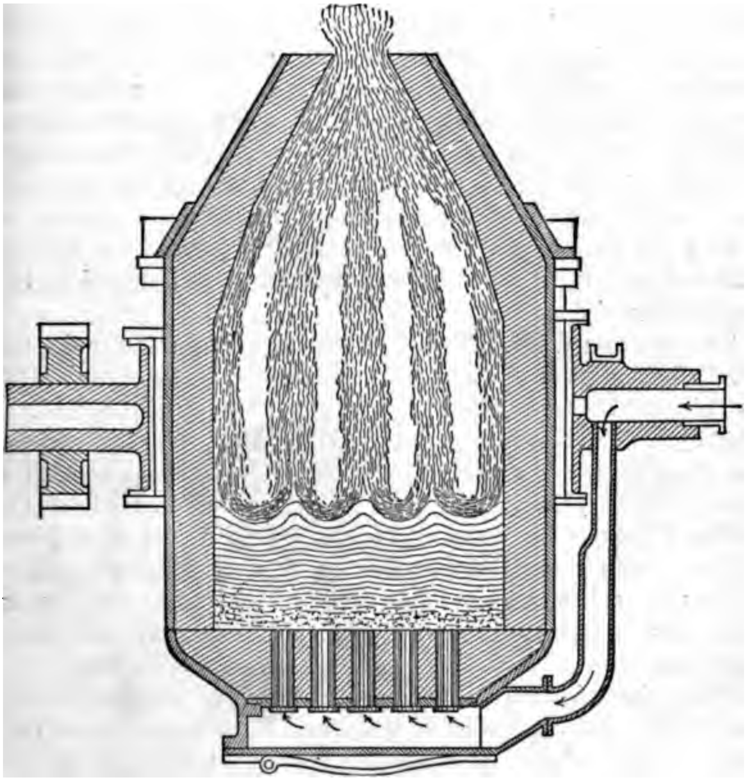

Fig. 72.

The converter used is a pear-shaped vessel, built of boiler plate and lined with silicious material, so mounted on trunions that it may be tipped through a very large angle, and provided with about 250 small holes in the bottom through which air may be blown (see Fig. 72). To start the blow, the converter is turned on its side and ten to fifteen tons of molten pig iro in.

The air is turned on and the converter straightened up so that the air passes through the molten iron, buring first the silicon to SiO_2, then the manganese to MnO, and lastly the carbon to CO. This burns at the mouth of the converter forming a great flame which gradually dies down and disappears at the end of the blow. The whole process is completed in from six to ten minutes. The heat produced raises the temperature some 300° which is favorable to the success of the operation, because removing the impurities raises the melting-point of the iron. By the time that the carbon is burned out, much of the iron is oxidized to FeO. This makes the product brittle and unfit for use. This fault is overcome by adding at the end of the blow such a quantity of spiegeleisen (an alloy of iron, manganese and carbon) as will furnish the manganese and carbon necessary to reduce the ferrous oxide and to bring the manganese, silicon, and carbon content of the whole mass to that required in the grades of steel desired.

This process using the acid or silicious lining leaves in the steel all the phosphorus and sulfur present in the pig iron. But by using basic linings made of lime or calcined dolomite, $CaCO_3 \cdot MgCO_3$, and adding lime with the charge, it is possible to remove the phosphorus and a part of the sulfur as calcium or magnesium phosphate or sulfide. The basic lining is less durable than the acid and the process more expensive, so it has been abandoned in America, although the properties of steel containing phosphorus or sulfur are so objectionable that only the purest and most expensive pig iron can be refined in acid lined converters.

After the addition of the spiegeleisen, the steel is poured out of the converter into a ladle and then tapped into cast iron moulds where it solidifies, forming ingots which are reheated and rolled into the shapes desired—rails, beams, rods, etc.

A very superior quality of steel can be produced by adding a small quantity of an alloy of iron and titanium soon after the addition of the spiegeleisen. The titanium completes the reduction of the oxides, combines with any nitrogen present, partially removes the phosphorus and sulfur, and greatly improves the strength, malleability, and toughness of the steel.

Open Hearth or Siemens-Martin Process. The open hearth process for steel making is even more important than the Bessemer as may be seen from the fact that this country produces yearly 16,500,000 tons by the former as against 9,400,000 tons by the latter. This is due largely to the fact that a basic lining may be economically used in an open hearth furnace, and hence steel may be cheaply made from pig iron which contains too much phosphorus for the acid Bessemer convertor.

The furnace used (see Fig. 73) is of the type known as regenerative because the air and the producer gas which is used as fuel are preheated by the waste heat of the escaping products of combustion, with the result that the temperature reached is very high.

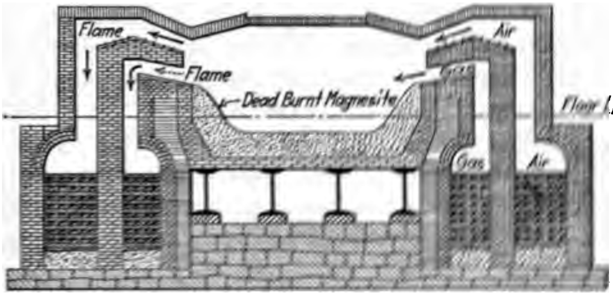

FIG. 73.

To secure these results, the air and gas are blown in separately through chambers filled with checkerwork of hot brick. They meet and burn just over the bed of the furnace containing the materials for forming the steel. The products of combustion pass out at the other side of the furnace through chambers which are duplicates of the ones through which the gases entered. In this way the checkerwork of brick in the exit chambers is intensely heated. After a time the direction of the passage of the gases through the furnace is reversed, and the brick in what had been the exit chambers now warms the incoming air and gas. This process is continued at regular intervals. Because of this preheating the temperature reached in the furnace is very high. This type of furnace was invented by Siemens Brothers and applied to steel-making by Martin, hence the name Siemens-Martin process.

The materials used are pig iron, soft scrap steel, iron ore and in the basic process, lime. The purification of the pig iron is effected partly by an excess of air in the flame which plays over the charge, but more by the oxidizing action of the iron oxide in the ore. When the oxide is reduced, it of course increases the amount of iron present. The scrap steel is added to dilute the impurities and so hasten the process. The lime makes a very basic slag in the [illegible] which calcium phosphate and calcium sulfide are [illegible] h the elimination of phosphorus and sulfur. Lime [illegible] sed only when the lining is made of calcium and m [illegible] de or the latter alone. The process is much slowe [illegible] essemer, requiring from six to ten hours, but the ca [illegible] he furnace is large, usually 50 to 75 tons. Bec [illegible] wness the changes can be followed by physica [illegible] ests, and hence a more uniform and higher gr [illegible] be produced than by the Bessemer converter. [illegible] ication, the charge is tapped out into a ladle, slag is removed as completely as possible, and the iron recarburized to the desired degree by the addition of ferromanganese (an iron alloy rich in manganese) and anthracite coal or charcoal. It is then cast into ingots and worked up as in the other process.

The acid process is used to make about 1,200,000 tons of the 16,500,000 tons produced in the open hearth. It differs mainly in using a silicious lining and omitting the lime from the charge. The materials used must be very low in phosphorus and sulfur.

Crucible Steel.—By melting wrought iron with a proper amount of charcoal or cast iron in large clay or graphite crucibles, a very fine grade of high carbon steel is made which is especially desirable for making tools, knives, springs, and other special uses. The steel made by this method usually has a carbon content of from 0.75 to 1.50 per cent. and is called crucible steel.

Electric furnace steel is practically the same as crucible steel. The main difference being that melting is carried out in an electric furnace instead of a crucible, and that larger charges can be worked at a lower cost. Because of the high temperature obtainable in these, they are often used to give Bessemer or open-hearth steel a super-refining which removes phosphorus nd sulfur, and greatly improves the quality. The electricity imply serves as a source of heat and there is no electrolysis in he process.

Within recent years, it has been found that the addition of one r more of the following metals to steel will increase its valuable ualities, or impart new ones; nickel, manganese, copper, chroium, vanadium, molybdenum, tungsten, titanium, and silicon; uch steels are called alloy steels, and are extensively used. langanese steel is very tough. Nickel increases the tenacity nd elastic limit. Chromium increases the hardness.

Wrought Iron.—A third method of purifying pig iron is the uddling process, invented by Henry Cort in 1784. This onsists in melting pig iron in small lots of 500 to 1,500 lb. in a everberatory furnace heated by coal or gas.

The hearth of the furnace is lined with roll scale or other aterial rich in iron oxide which with the excess oxygen in the urnace gases, serves to oxidize silicon, manganese, carbon, phoshorus and sulfur. The silica, manganous oxide, and phoshorous pentoxide produced, unite with some iron oxide formed y oxidation of iron, making a very basic slag, and effectually emoving them from the iron. The melting-point of the iron hich is about 1,200° in the impure state at the beginning, gradully rises as the impurities are eliminated and finally becomes o high that the pure iron cannot remain liquid at the highest emperature of the furnace. It separates, therefore, as a spongy lastic mass, honey-combed with slag. This is gathered together nd worked into balls weighing about 125 lb., which are then emoved from the furnace and passed through a mechanical queezer to expel slag. The iron is rolled into rough bars, which re cut up, piled together, reheated to welding temperatures, nd rolled into bars and other shapes.

The product of the puddling furnace, called wrought iron, is ery nearly free from impurities, other than slag, and is the purest ommercial iron.

It is very soft and malleable, welds easily, and is characterized y a fibrous structure, which easily distinguishes it from low arbon steel, which is rolled into form from cast ingots nearly ree from slag. This structure is due to particles of s nclosing hose of iron and c iron particles to ly during the rolling process. The fibrous structure, it is thought, increases the strength of the iron.

Physical Properties of Iron.—Pure iron is the most magnetic of the metals. It has a density of 7.8, is silvery white, takes a high polish and is very ductile and malleable. It may be welded at a bright red heat and melts at 1,505°.

Pure iron is soft and cannot be hardened, but steel can be hardened by heating t erature and suddenly cooling in water. If thi el is reheated, it may be softened or tempered a The explanation is found in the fact that iron forr $_3$C, called cementite which is soluble to a limited at temperatures above 725° forming solid solutio bility increases with the temperature reaching arbon at 1,145°. If these solid solutions are qu y plunging the steel into water, the cementite olution, and the resulting solid solution is hard. The mo mentite in the solution the harder the steel is. If this hardened steel be reheated, the cementite begins to separate and the steel gets softer. By controlling the temperature and the duration of reheating, the steel may be brought to any desired degree of hardness between that of the chilled steel and that of pure iron. The softening process may be stopped at any point by suddenly cooling the steel. Experienced workmen judge the hardness by the colors of the film of oxide on the steel which are a rough measure of the temperature to which the iron is heated.

Chemical Properties of Iron.—Iron is stable in dry but is attacked by moist air and gradually becomes covered with iron rust, $2Fe_2O_3·3H_2O$, which does not protect the underlying metal from further action. Something of a discussion of the mechanism of the rusting of iron will be given at the close of the treatment of this metal. When heated in the air or steam, iron becomes converted into the magnetic oxide, Fe_3O_4, which when formed under certain conditions clings tightly to the surface of the metal and protects it from further oxidation (Baruff's process for the prevention of rust). Dilute hydrochloric or sulfuric acids dissolve iron with the evolution of hydrogen and the formation of ferrous salts: the hydrogen usually contains some hydrocarbons as well as compounds of phosphorus and sulfur and has a disagreeable odor. When the iron dissolves in cold dilute nitric acid, ferrous nitrate and ammonium nitrate are formed; while with somewhat more concentrated acid, ferric nitrate and oxides of nitrogen are produced. When iron is dipped into very concentrated nitric acid, it almost instantly becomes passive, that is passes into a condition in which it is not attacked by nitric acid, dilute or concentrated, and does not precipitate copper from cupric solutions. In fact, it acts as though it were moved in the potential series to a position near that of platinum. Potassium dichromate, chloric, bromic, iodic acids and other powerful oxidizing agents will also induce the passivity of iron. There is no visible change in the iron. The passivity is destroyed by contact with reducing agents, scratching the surface or even by simply placing the iron in a very strong magnetic field. An entirely consistent and satisfactory explanation of this phenomenon is lacking.

Ferrous Compounds.—The ferrous compounds are very much like those of magnesium and especially like manganous salts with the exception that the trivalent compounds of iron are more stable than the divalent either in acid or alkaline solution, while the reverse is true for manganese in acid solution. The ferrous salts even in acid solutions are oxidized in the air to ferric; in alkaline solutions, the change takes place more readily. When a perfectly pure ferrous salt solution is acted upon by a soluble base in the entire absence of oxygen, a white precipitate of **ferrous hydroxide,** $Fe(OH)_2$, is obtained. On exposure to the air, it becomes first dirty green and finally brown from oxidation to ferric hydroxide. Ferrous hydroxide has about the solubility and strength of magnesium and manganous hydroxides and hence, like these is soluble in an excess of ammonium salts and for the same reason. It is not soluble in excess of the alkalies or of ammonium hydroxide, but is, of course, in acids. From its solubility in ammonium salts, it follows that it is a fairly strong base and its salts are but little hydrolyzed, so those of even as weak an acid as carbonic can be easily prepared. **Ferrous oxide,** FeO, corresponding to the hydroxide is most easily made by heating the oxalate in the absence of air. It has a black color.

Ferrous Sulfate.—Ferrous sulfate, $FeSO_4{\cdot}7H_2O$, is the best known and most largely used of the ferrous salts. In its crude form it is often called green vitriol or copperas. It is made on a very large scale by the oxidation of moist pyrite.

$$2FeS_2 + 7O_2 + 2H_2O = 2FeSO_4 + 2H_2SO_4$$

The ferrous sulfate and sulfuric acids which are formed are leached out, the acid is allowed to act on scrap iron, and the solution concentrated to cr Rather large quantities of ferrous sulfate are obtain oduct in plants where there is occasion to clean or ' urface of much iron by the action of sulfuric acid.

The sulfate is used as it and disinfectant, in the manufacture of dyes, in ta the making of inks, and in the clarification of water.

Ferrous Sulfide.—I eS, is formed by the direct union of the elements. lace very readily when the two are heated together. has a slight metallic luster. It is readily dissolved by hydrochloric or sulfuric acid with the formation of hydrogen sulfide and the corresponding ferrous salt. The usefulness of hydrogen sulfide as a reagent makes ferrous sulfide important also. It is precipitated by ammonium sulfide as a black powder easily soluble in acids, but is not precipitated by hydrogen sulfide from acid solutions.

Other Ferrous Compounds.—**Ferrous chloride,** $FeCl_2$, is much more soluble than ferrous sulfate, and on this account it is advisable to use hydrochloric acid instead of sulfuric in the generation of hydrogen sulfide, as the apparatus is not so likely to become clogged with crystals of the salt. There is nothing especially noteworthy concerning the **bromide** and the **iodide** except that ferrous iodide is the only stable iodide of iron, the ferric salt decomposing into the ferrous and free iodine. **Ferrous carbonate** occurs in nature as spathic iron ore. As it is obtained in the laboratory, it is partially hydrolyzed and is easily oxidized to the ferric hydroxide. It is more soluble in water containing carbon dioxide in solution than in pure water.

Ferric Compounds.—As has been mentioned, the ferric compounds are formed from the ferrous by oxidation. This takes place more readily in alkaline than in acid solutions, but oxygen of the air is able to bring about the chan
case.

Any ferric salt in solution will be reduced to the ferrous state by the stronger reducing metals such as zinc, magnesium, iron, etc.; or by hydrogen sulfide, stannous chloride, or iodine as ion. Some of these properties are made use of in the quantitative determination of iron, it being reduced to the ferrous state and then titrated with permanganate.

Ferric Hydroxide.—Solutions of bases when added to a solution of a ferric salt, produce a brown precipitate of ferric hydroxide, $Fe(OH)_3$. This precipitate is very slimy when formed in the cold, but becomes more compact upon boiling. It has a marked tendency to pass into colloidal solution especially in the presence of ferric chloride. By separating such a solution from pure water by parchment paper, dialysis will take place and the ferric chloride will gradually diffuse into the water leaving a pure solution of colloidal ferric hydroxide. This is called dialyzed iron and has a strong red color. Like other colloids it has practically no effect upon the boiling-point of the water, and is precipitated by many neutral salts. It is a positive colloid and di- and trivalent anions are much more effective than monovalent ones. Ferric hydroxide is soluble in acids, but not in excess of dilute alkalies; or in ammonia or ammonium salts. It is a very weak base, and its salts are as highly hydrolyzed as the salts of aluminum; hence, their solutions are decidedly acid. The ferric ion appears to be colorless, but the ferric salt solutions are usually colored, presumably, in most cases, from the hydroxide formed by hydrolysis.

When the hydroxide is dried and heated, it passes into ferric oxide, Fe_2O_3, which in finely divided condition is known as "rouge" and "Venetian red," and is used as a polishing material and pigment. Although ferric hydroxide will not dissolve in dilute alkalies it is somewhat soluble in very concentrated solutions of sodium or potassium hydroxide, forming unstable ferrites. The dark colored substance formed during the early stages of the oxidation of ferrous hydroxide is probably a hydrated ferrous ferrite; and magnetic iron oxide, Fe_3O_4, is in all probability the anhydrous compound and should be written $Fe(FeO_2)_2$. This is a valuable iron ore and remarkable because of its being attracted by magnets. Some specimens act as magnets and are then known as lodestones. Calcium, magnesium, and zinc ferrites of the general formula $M(FeO_2)_2$, are known. These like the ferrous ferrite are magnetic.

Ferric Chloride.—When chlorine is passed over heated iron, anhydrous ferric chloride, $FeCl_3$, sublimes and crystallizes in dark green scales which have a metallic luster and are red by transmitted light. It dissolves in water with the evolution of heat and from the solution a number of hydrates may be obtained, the most [illegible] $FeCl_3 \cdot 6H_2O$. This is most readily prepared, [illegible] ous chloride with chlorine, evaporating the so [illegible] he composition of the hexahydrate and allow [illegible] The hydrate melts at 37° and is very soluble [illegible] Solutions of ferric chloride are considerably h [illegible] at high temperatures than at low, and react str [illegible] chloride is soluble in alcohol and ether as well a [illegible] used in medicine.

Ferric Sulfate.— [illegible] $_2(SO_4)_3$, may be prepared as a yellowish white solid b [illegible] e proper amount of sulfuric acid to ferrous sulfate in solution and then oxidizing with nitric acid,

$$6FeSO_4 + 3H_2SO_4 + 2HNO_3 = 3Fe_2(SO_4)_3 + 2NO + 4H_2O$$

and evaporating to dryness. With potassium and ammonium sulfates, it forms alums such as ammonium iron alum, $NH_4Fe(SO_4)_2 \cdot 12H_2O$. When pure these are almost colorless, but generally have a violet tint due perhaps to the presence of a trace of manganese. Basic ferric sulfates are known and are used in medicine to stop the flow of blood from wounds.

Ferric Thiocyanate.—Ferric thiocyanate, $Fe(NCS)_3$, is a slightly dissociated salt which is formed by the interaction of a ferric salt and a soluble thiocyanate. It has a most intense blood red color which is visible even at high dilutions. The appearance of this color upon the addition of potassium thiocyanate is a very delicate test for ferric iron. Pure ferrous compounds give no color.

Ferric Sulfide.—Ferric sulfide, Fe_2S_3, is thrown down as a black precipitate when a ferric salt is added to an excess of ammonium sulfide, but when the ferric salt is in excess, reduction takes place with the formation of ferrous sulfide and sulfur. Ferric sulfide is also formed by the direct union of the elements.

Pyrite.—Pyrite or "Fool's gold," FeS_2, is the most stable of the sulfides of iron at ordinary temperatures. It is found in very large quantities in nature and is an important source of the sulfur for sulfuric acid. It occurs in golden colored crystals which appear in a great variety of forms belonging to the regular systems, cubes and octahedrons being common.

Ferric Phoshate.—Ferric phoshate, $FePO_4$, is so slightly soluble that it is precipitated upon the addition of sodium phosphate to a ferric solution even in the presence of acetic acid in which most phosphates are soluble. Advantage is sometimes taken of this property to remove the phosphate ion from solutions. It is a white slimy precipitate soluble in strong acids.

Cyanogen Compounds.—When potassium cyanide is added to a ferrous solution a yellow precipitate is formed which is ferrous cyanide. It dissolves in an excess of potassium cyanide, forming the typical complex salt, potassium ferrocyanide or yellow prussiate of potash, $K_4Fe(NC)_6$. This is easily soluble in water and the solution shows the properties of other potassium salts, but not those of either the ferrous salts or the cyanides; on the contrary, it has an entirely different set of properties. The salt for example is nothing like as poisonous as potassium cyanide. This is expressed by saying that it dissociates into potassium as ion and the complex ferrocyanogen ion, $Fe(NC)_6^{----}$. This ferrocyanogen ion is formed whenever the ferrous ion is boiled with the cyanogen in alkaline solution. The potassium salt has the composition, $K_4Fe(NC)_6 \cdot 3H_2O$, and the sodium, $Na_4Fe(NC)_6 \cdot 10H_2O$. Many of the ferrocyanides are insoluble and may be prepared by precipitation. Ferric ferrocyanide, $Fe_4(Fe(NC)_6)_3$, has a dark blue color and is known as "Prussian blue." The formation of this dark blue precipitate is a very delicate test for ferric iron and it is indeed remarkable that a solution containing iron can be used as a reagent for iron. When potassium ferrocyanide is added to a ferrous salt solution in the absence of oxygen, a white precipitate having the composition, $K_2FeFe(NC)_6$, is formed which quickly oxidizes and becomes blue.

Ferricyanides.—Ferricyanides may be easily formed from the ferrocyanides by the action of oxidizing agents. The potassium salt, $K_3Fe(NC)_6$, for example is made by passing chloride through a solution of potassium ferrocyanide,

$$2K_4Fe(NC)_6 + Cl_2 = 2KCl + 2K_3Fe(NC)_6$$

It crystallizes in dark red prisms and is known as "red prussiate of potash." It is the potassium salt of the complex ferricyanogen ion, $Fe(NC)_6^{- - -}$, which differs from the ferrocyanogen in that it carries one less – charge. Ferric salts do not give any precipitate with ferricyanides, but the solution becomes somewhat dark brown. Ferrous salts, however, react and produce a dark blue precipitate of Turnbull's blue, ferrous ferricyanide, $Fe_3(Fe(NC)_6)_2$; which is very similar to Prussian blue. In fact, some consider it identical with Prussian blue and think that ferricyanogen oxidizes the ferrous ion to the ferric- and is itself reduced to the ferrocyanogen before they combine.

When solutions of potassium ferricyanide and ammonium ferric citrate are mixed, a yellowish-brown liquid results. If this be spread over paper and the latter dried in the dark, sensitized **blue print** paper results. When it is exposed to sunlight under a tracing or negative, it turns blue wherever the light strikes the paper, from the formation of insoluble blue compounds like Prussian blue. This may be due to the reduction of the ferric salt to the ferrous or of the ferricyanogen ion to the ferrocyanogen and then their interaction. After the printing, the picture is "fixed" by washing in water which dissolves the unchanged mixture, leaving white lines on a blue ground.

Oxalates.—Ferrous oxalate, FeC_2O_4, is precipitated as a yellow salt by the addition of oxalic acid to a ferrous solution. It is soluble in potassium oxalate owing to the formation of the complex salt, $K_2Fe(C_2O_4)_2$, which has a yellowish-red color not unlike that of many ferric salts. Ferric oxalate, unlike other ferric salts, has a green color remotely like that of the ferrous salts. It forms a stable complex salt with potassium oxalate, $K_3Fe(C_2O_4)_3$, which also has a green color and gives the complex ion $Fe(C_2O_4)_3^{- - -}$. The usefulness of oxalic acid and of acid potassium oxalate in removing rust and ink spots from fabrics is due to the formation of this complex ion. Solutions of ferric oxalate and of its complex compounds are very sensitive the light and are quickly reduced to ferrous oxalate with the evolution of carbon dioxide.

Ferrates.—When ferric hydroxide is suspended in potassium hydroxide solution and chlorine passed in, a red solution of potassium ferrate, K_2FeO_4, is formed. This may be obtained as crystals isomorphous with potassium sulfate and chromate. It is very unstable. Other salts have been prepared by precipitation.

The Corrosion of Iron.—It is, of course, well known to everyone that iron when exposed to air and water will gradually be converted into partially dehydrated ferric hydroxide, which is called iron rust. The importance of an understanding of the conditions which influence this change is obvious, owing to the almost universal use of iron in our modern structures. There is a good deal of dispute concerning many of the facts in connection with this and still more as to their interpretation, but the following observations are generally accepted as facts. First, iron will be rapidly dissolved and corroded by practically all dilute acids including carbonic, solutions of ferrous salts and hydrogen gas being the usual products. Second, iron will slowly dissolve in pure water even in the absence of oxygen or carbon dioxide. The action is not very extensive, but hydrogen gas is evolved and the solution becomes distinctly alkaline from the ferrous hydroxide which is dissolved. In the entire absence of air, the solution of ferrous hydroxide formed by the action of distilled water upon iron will remain clear; but if air be passed through it, the whole solution will take on the color of iron rust and will deposit it. Third, that the corrosion of iron will be greatly increased by the presence of oxygen. Fourth, that the iron is more readily attacked the more impure and non-homogeneous it is. Fifth, that in alkaline solutions the corrosion is greatly hindered or suppressed. Sixth, that in certain strong oxidizing agents, such as concentrated nitric acid, dichromates, and red lead, the iron becomes "passive" and will retain this condition for some time after the removal of the oxidizing agent.

The most consistent interpretation of these facts seems to be the following: That the oxidation of the iron takes place in two stages; first, to the ferrous and then to the ferric condition; that the oxidizing agent which dissolves the ir ous state is hydrogen as ion either from acids or from water, and that the oxidation to the ferric is brought about by the oxygen of the air. Since an oxidizing agent is the more active the more concentrated it is, the more rapid solution in acids than in water is readily understood as being due to the smaller concentration of the ionized hydrogen in the latter. The protective action of alkaline solutions may be ascribed to the concentration of the hydrogen as ion hav [illegible] duced by the increase in the concentration of t [illegible] it is not a strong enough agent to oxidize the [illegible] e first stage of the rusting cannot take place.

If the iron is non [illegible] ltaic couples will be set up at various points on [illegible] ocal electrolytic action will result. Hydrogen [illegible] sited at those points where the metal for any c [illegible] is [illegible] thode, and since this hydrogen has a tendency t [illegible] solution as ion, the local cells will be polarized and [illegible] lered. If oxygen is present, it will act as a depolarizer [illegible] increase the rate of electrolytic corrosion, and then in addition will oxidize the ferrous ion so produced to the ferric, and so complete the rusting process. There seems to be no satisfactory explanation for the passivity of iron.

Analytical Properties of Iron.—Because of the precipitation of ferric hydroxide by ammonium hydroxide in the presence of ammonium salts, iron is placed in an analytical group with aluminum and chromium. Ferrous salts give a deep blue with ferricyanides, while ferric compounds give the same color with ferrocyanides and also a blood red with thiocyanates. With the borax bead, iron compounds give green colorations in the reducing flame and a faint yellow or brown in the oxidizing flame.

COBALT

Cobalt has a slightly higher atomic weight than nickel, but it is more closely related to iron than nickel is, so it is usually placed ahead of the latter in the periodic system. Cobalt occurs in nature in rather small quantities chiefly as smaltite, $CoAs_2$, and cobaltite, CoAsS, and is commonly associated with iron, nickel, and manganese. It is almost always a constituent of meteoric iron and is present in the sun as indicated by the spectrum. The metal may be obtained by the reduction of the oxide at a high temperature with carbon or hydrogen, by the Goldschmidt process, or by the electrolysis of a solution of the sulfate. It is magnetic and has the color of polished iron, becoming pink on exposure to the air, and melts at 1,494°. It slowly oxidizes when heated and burns at a high temperature. It is attacked by dilute acids, but tends to become passive as iron does. Very recent experiments indicate that cobalt can be substituted with advantage for nickel in electroplating other metals. The coating may be applied much more rapidly, it is harder and more durable and hence may be made thinner than nickel with equally good results. Cobalt forms two series of compounds corresponding to ferrous and ferric. The simple cobaltous compounds are more stable than the simple cobaltic, but the case is the other way around with the complex compounds.

Cobaltous Compounds.—When sodium hydroxide is added to a cobaltous solution, a blue precipitate of basic salt is formed which on standing becomes pink and is changed to the **hydroxide**, $Co(OH)_2$. This, like the corresponding ferrous, manganous, and magnesium compounds, is soluble in ammonium salts. In addition, it is soluble in ammonium hydroxide presumably because of the formation of complex ammonia ions. The ammoniacal solution absorbs oxygen, and a series of complex cobaltic ammonia salts are formed which will be treated briefly a little later. The cobaltous salts in dilute solution have a red color and so do most of the fully hydrated solid salts, but the partially or completely dehydrated compounds are generally blue. **Cobalt chloride,** $CoCl_2 \cdot 6H_2O$, is especially sensitive in this respect. One may prepare a dilute solution of cobalt chloride and write with it upon paper; after drying, the delicate pink of the salt is scarcely visible, but when heated it loses water and the characters become distinctly traced in the blue of the less hydrated salt. Upon standing in the air at ordinary temperatures, the salt takes up water once more and the writing disappears. This is the basis of the so-called "sympathetic ink."

Cobalt Sulfate.—Cobalt sulfate, $CoSO_4 \cdot 7H_2O$, is isomorphous with magnesium sulfate and forms double sulfates with ammo-will not be described here, but something will be said of one method in connection with nickel carbonyl.

Properties.—Nickel is a silvery white metal with a tinge of yellow. It takes a high polish and is hard but malleable and may be rolled into thin sheets or drawn into fine wire. The pure metal melts at 1,451°. It is magnetic. Nickel is a component of a number of important alloys. German silver contains approximately 60 per cen per cent. zinc, and 15 per cent. nickel, but the aries widely. Nickel coins usually contain 75 , and 25 per cent. nickel. Nickel steel has ve ties because of its increased strength and toughn aining about 36 per cent. of nickel has a very s coefficient and is known as "invar." It is use dard meters because their length will vary but temperature. A complex wire having a core acket of copper and a coat of platinum over al ller coefficient of expansion than glass and is coming place of the very precious metal platinum for sealing in wires in electric light bulbs. Monel metal is a nickel-copper alloy obtained by the direct smelting of the nickel copper ores mined at Sudbury, Ontario. It can be cheaply produced and has the very valuable properties of corroding less easily than brass or bronze and of being nearly as strong as steel. Nickel may be readily deposited electrolytically from a solution of the double sulfate with ammonia $(NH_4)_2Ni(SO_4)_2 \cdot 6H_2O$, using anodes of cast nickel containing some carbon because they dissolve more readily than the pure metal. Iron or steel articles are first coated with copper and then with nickel. Nickel plate takes a high polish and protects the iron effectually from rust. Nickel does not rust in the air and is but slowly attacked by steam even at a red heat. It is slowly dissolved by dilute acids with the exception of nitric which acts upon it rapidly. Concentrated nitric acid, however, renders it passive.

Nickel Compounds.—Nickel forms only one series of salts which correspond to the ferrous and cobaltous salts. These may be considered to be derived from the oxide, NiO, or the hydroxide, $Ni(OH)_2$, both of which are well-known. In addition there is a well-defined oxide, Ni_2O_3, and a hydroxide, $Ni(OH)_3$, corresponding to ferric oxide and hydroxide, Ni_3O_4, analogous to magnetite, and a peroxide, NiO_2, but no salts of these are known. The nickel salts both in the crystalline form and in solution are usually green.

Oxides and Hydroxides.—Nickelous hydroxide, $Ni(OH)_2$, is an apple green precipitate. When heated, it readily decomposes into water and the oxide, NiO. The hydroxide is not soluble in an excess of sodium hydroxide, but does dissolve in ammonium hydroxide owing to the formation of dark blue nickel ammonia ions which probably have the composition, $Ni(NH_3)_4{}^{++}$, and $Ni(NH_3)_6{}^{++}$. The hydroxide is also soluble in ammonium salts. Nickelic oxide, Ni_2O_3, may be obtained by carefully heating the nitrate. When this or any of the other compounds of nickel is heated in oxygen, the oxide Ni_3O_4 is formed. Nickelic hydroxide, $Ni(OH)_3$, is a black precipitate which is formed by the action of a hypochlorite on any nickel salt in solution. When nickelic hydroxide or any of the oxides, higher than the monoxide, is dissolved in hydrochloric acid, chlorine is evolved and nickelous chloride, $NiCl_2$, is formed.

Edison Storage Cell.—The Edison storage battery is a reversible, electric cell in which the oxidizing agent is nickelic hydroxide, $Ni(OH)_3$; the reducing agent finely divided iron; and the electrolyte 21 per cent. potassium hydroxide. While it is discharging, the nickel is reduced to the divalent state, and the iron oxidized to the ferrous. On charge the nickel is oxidized to the nickelic, and the ferrous reduced to the metallic state, thus restoring the cell to its original condition. Its electromotive force is lower and its internal resistance higher than the corresponding magnitudes for the lead storage cell, so it is less efficient, but it is lighter and more durable than the latter.

Salts.—Anhydrous nickel chloride is brown, but the hexahydrate, $NiCl_2 \cdot 6H_2O$, is green like most of the nickel salts. The sulfate usually crystallizes as a hexahydrate, $NiSO_4 \cdot 6H_2O$, but it may be obtained as heptahydrate isomorphous with magnesium sulfate. The double sulfate with ammonium sulfate, mentioned in connection with nickel plating, is isomorphous with the other double sulfates of this same type. It is manufactured on a large scale and is one of the important salts of nickel. Nickel cyanide, $Ni(NC)_2$, is a green precipitate which is thrown down by potassium cyanide from a nickel salt solution

It is soluble in an excess of the potassium cyanide forming the complex salt, $K_2Ni(NC)_4 \cdot H_2O$. This is not analogous to ferro- and cobaltocyanides and is much less stable. It is not oxidized to anything which corresponds to the ferri- or cobalticyanides. Nickel salts color the borax bead brown while cobalt compounds give a very intense blue. Nickel sulfide, NiS, is formed under the same conditions as that of cobalt and has the same solubility. A solution glyoxime $H_2O_2N_2C_2(CH_3)_2$, reacts with a solutic salt, acid with acetic acid and containing sod give a bright red precipitate of nickel dimethyl

$NiCl_2 + 2H_2O_2N_2C$ $H_3O_2 = Ni[HO_2N_2C_2(CH_3)_2]_2$
$C_2H_3O_2$

Cobalt does not ecipitate and this makes it easy to detect nick of cobalt.

Nickel Carbonyl.—Nick yl, $Ni(CO)_4$, is formed below 80° by the action of carbon monoxide upon finely divided nickel. It is a colorless liquid which boils at 43°. Its vapor decomposes explosively at 60°. When diluted with carbon monoxide it decomposes gradually and its decomposition is not complete below 180°. Cobalt does not form any similar compound. A process based upon this property of nickel has been used for its extraction from the ores. One difficulty in its application is that the carbon monoxide is partially decomposed with the deposition of carbon and the formation of the dioxide.

THE PLATINUM METALS

The remaining members of Group VIII, the ruthenium and platinum sub-groups may conveniently be considered together under the heading of the platinum metals. These metals are found associated in the native platinum ores which are obtained by placer mining or dredging, chiefly in the Ural Mountains, although Columbia furnishes a small per cent. of the world's output. They are also found in certain copper ores and in the nickel copper ores of Sudbury, Ontario. In the following t these metals are arranged as they are in the periodic system a under each is given some of its more prominent properties and the formulas of a few typical compounds.

	Ruthenium		*Rhodium*		*Palladium*	
Density	12.0		12.1		11.5	
Melt. p.	2,000°		1,970°		1,550°	
Oxides	RuO		RhO		PdO	
	Ru_2O_3		Rh_2O_3		———	
	RuO_2		RhO_2		PdO_2	
	RuO_4	(vol. liq.)	———		———	
Salts	$RuCl_2$		———		$PdCl_2$	
	$RuCl_3$,	K_3RuCl_6	$RhCl_3$,	K_3RhCl_6	———	
	———		$Rh_2(SO_4)_3$	(alums)	———	
	$RuCl_4$,	K_2RuCl_6	———		$PdCl_4$,	K_2PdCl_6
	K_2RuO_4,	$KRuO_4$	———		———	
	Osmium		*Iridium*		*Platinum*	
Density	22.5		22.4		21.4	
Melt. p.	2,700°		2,200°		1,753°	
Oxides	OsO		———		PtO	
	Os_2O_3		Ir_2O_3		———	
	OsO_2		IrO_2		PtO_2	
	OsO_4	(vol. liq.)	———		———	
Salts	$OsCl_2$		$IrCl_2$		$PtCl_2$,	K_2PtCl_4
	$OsCl_3$,	K_3OsCl_6	$IrCl_3$,	K_3IrCl_6	———	
	———		$Ir_2(SO_4)_3$	(alums)	———	
	$OsCl_4$,	K_2OsCl_6	$IrCl_4$,	K_2IrCl_6	$PtCl_4$,	K_2PtCl_6
	K_2OsO_4					

An inspection of this table will show strong resemblances between the elements in each horizontal row and vertical column. All these elements form complex compounds with ammonia which are so numerous and varied that larger works must be consulted for their discussion.

Ruthenium and **osmium** are iron gray metals which are not dissolved by any single acid, and are but very slowly attacked even by aqua regia. They are dissolved by fusion with alkalies and nitrates. When finely divided and heated in oxygen they form the tetroxides and volatilize. Osmium tetroxide is not the anhydride of any acid, but is called osmic acid. It is used for staining and hardening histological specimens. It has a very disagreeable odor and is exceedingly irritating to the mucous membrane owing to its reduction to metallic osmium. The formation of osmates and ruthenates establishes a connection with iron and manganese.

Rhodium and iridium are white metals which are not attacked by aqua regia. They will form very hard, chemically resistant alloys with platinum. Iridium especially is used for this purpose.

Palladium and platinum are white metals. Platinum dissolves in aqua regia and palladium even in nitric acid, and is the only metal in the two sub-groups which will do so. Both platinum and palladium are remarkable for their ability to absorb gases, especially hydrogen, of which palladium will take up as much as 1,000 times its volume. The hydrogen and the palladium form a solid solution which has greater volume than the metal. The hydrogen in this solution will readily reduce silver and copper to the metals, and ferric salts to ferrous as would be expected from the position of hydrogen in the potential series, which, of course, is not materially altered by its solution in palladium.

Platinum.—Platinum is by far the most important member of this group. Not only is it indispensable to the chemist, but it also touches our daily life in many ways, especially in our electrical appliances. It is almost the only pure metal which has the proper coefficient of expansion, melting-point, and chemical resistivity to enable it to be fused through glass. This comes into play in many ways, particularly in the making of incandescent electric bulbs. It is used in the form of wire, foil, crucibles, and dishes in the laboratory, and it is hard to conceive what we should do without it.

Platinum ware must be handled with care because it is ruined by contact when hot with easily fusible metals, alkalies, phosphorus, carbon, and silicon. The carbonates of the alkalies may be heated in it without danger. Aqua regia or anything which will evolve chlorine should not be allowed in contact with platinum.

As has been noticed many times on the preceding pages, platinum is very active as a catalytic agent, especially for reactions between gases. Advantage is taken of this on a large scale for the production of sulfuric acid by the contact process. The reactions take place on the surface of the metal and naturally go on more rapidly in the aggregate, the greater the surface exposed. For this reason the very finely divided black form of the metal which is obtained by the electrolysis of its chloride in solution, or by the reduction of the solution with a powerful reducing agent, is especially active and will cause the instantaneous explosion of a mixture of oxygen and hydrogen. The metal may be obtained in a spongy condition with large surface and high activity by gently heating ammonium chloroplatinate, $(NH_4)_2PtCl_6$, which decomposes and leaves spongy platinum. By heating this platinum sponge to whiteness and then hammering, it may be converted into compact metal, for at this temperature platinum welds very easily.

Platinum Compounds.—As may be seen from the table, platinum forms two series of compounds. In the platinous it is di- and in the platinic tetravalent. The platinous compounds are generally formed from the platinic by reduction.

Platinous Hydroxide.—Platinous hydroxide, $Pt(OH)_2$, is a black precipitate which is soluble in acids but not in bases. With hydrochloric acid it forms chloroplatinous acid, H_2PtCl_4, whose potassium salt, K_2PtCl_4, potassium chloroplatinite is used in making platinum photographic prints. Similar compounds are well known in which chlorine is replaced by cyanogen. These are called platinocyanides. The barium platinocyanide, $BaPt(NC)_4 \cdot 4H_2O$, is very fluorescent and shines under the influence of ultra-violet light and X-rays. Advantage is taken of this in making screens for X-ray work.

When platinum dissolves in aqua regia it forms **chloroplatinic acid**, H_2PtCl_6, which gives sparingly soluble chloroplatinates with potassium and ammonium salts, K_2PtCl_6, and $(NH_4)_2PtCl_6$. These form yellow precipitates which consist of small octahedrons and are very characteristic for platinum. When heated they decompose and leave spongy platinum and potassium chloride from K_2PtCl_6, or simply platinum from the ammonium salt. When silver salts are added to solutions of the chloroplatinates, precipitates of Ag_2PtCl_6, are formed and not AgCl, which shows that the chloroplatinate ion is a stable complex ion. By heating chloroplatinic acid in a stream of chlorine, platinic chloride, $PtCl_4$, is formed. When dissolved in water this gives H_2PtCl_4O.

Platinic Hydroxide.—Platinic hydroxide, $Pt(OH)_4$, is formed by the addition of bases to chloroplatinate solutions. It is soluble both in acids and bases. Complex platinates are for the action of bases upon the hydroxide. The potassium salt may be represented by the formula, $K_2Pt(OH)_6$, and is considered analogous to the chloroplatinates.

Analytical Properties of Platinum.—Platinous sulfide, PtS, and platinic sulfide, PtS_2, are precipitated by hydrogen sulfide from the respective salts. They are not soluble in dilute acids but dissolve in yellow [illegible] ide, forming thioplatinates. Platinum compounds [illegible] uced to the metal by ferrous salts but not by oxal [illegible] tter property is a distinction from gold.

CHAPTER XXXI

RADIOACTIVITY

In discussing radium, thorium, and uranium, mention was made that these substances are radioactive; and by this is meant that they spontaneously give out heat and other manifestations of energy which are able to affect a photographic plate; to cause certain substances to fluoresce; and to render the air in their neighborhood a conductor of electricity. These other manifestations of energy are called rays; and from this comes the term radioactivity. Three different kinds of these rays are distinguished; the alpha, beta, and gamma rays.

The alpha rays are responsible for most of the ionization of the air produced by radioactive substances; they can penetrate the air only a few centimeters and are easily stopped by paper. They are connected with the development of the greater part of the heat evolved by such substances. When uninfluenced by external forces they move in straight lines; but under the influence of an electrostatic or a magnetic field, they are slightly bent out of their path and act as though they consisted of a stream of rapidly moving small particles charged with positive electricity. Calculations based upon the bending of the path of the rays in these two fields indicate that 2 grm. of the rays would carry 96,500 coulombs and that they move with about one-tenth the velocity of light. These rays are generally supposed to be atoms of helium carrying two positive charges of electricity.

The beta rays are more penetrating than the alpha rays and pass readily through paper and even through thin sheets of metal. They are especially active toward a photographic plate. Like the alpha rays they move in a straight line, unless influenced by a magnetic or electrostatic field when they are deflected in the opposite direction from that in which the alphas are turned and much more strongly. They act like negatively charged particles, and calculations based upon this assumption indicate that 1 grm.

of beta rays would carry 1,800 × 96,500 coulombs and move with velocities varying from one-third to almost equal that of light. These rays appear to be identical with the cathode rays of a high vacuum tube. The very small particles which constitute these rays are called electrons.

The gamma rays are very penetrating and will pass readily through bodies which will stop the other forms of radiations. They are produced in much smaller amounts than the other rays. They are no[illegible]gnetic or electrostatic fields and seem to be ide[illegible]rs, that is they are light of exceedingly short wav[illegible]uch shorter than that which is visible. They are [illegible]uced by the impact of the beta rays.

Certain experim[illegible] performed with the α-rays which furnish the str[illegible]e yet brought forward that particles of about the [illegible]e of the atoms really exist. These experiments may [illegible]d as follows: A source of α-rays is placed at [illegible]om and in line with a brass tube. In the axis [illegible] insulated from it is a wire connected with an electrometer. [illegible]here is a high difference of potential between the tube and the wire. As the α-rays enter the tube, they render the air within it a conductor and the needle of the electrometer moves. If the radioactive substance is far enough from the tube, the movement of the electrometer is intermittent and the jumps come at intervals of a few seconds. This shows that the stream of α-particles is not continuous, or the movement would have been steady. By counting the jumps it is possible to determine the number of particles entering the tube in unit time. If now an insulated plate of metal the size of the opening in the tube be placed at the mouth of the latter, it will absorb the α-rays and take up the charge of electricity that they carry. By determining the charge acquired in unit time, the charge on one particle can be calculated, and from this, assuming that the α-particles are helium atoms, since 4 grm. of α-particles carry 2 × 96,500 coulombs, the number of particles in a gram mole of helium and the mass of a single molecule may be calculated. The results are that a gram mole contains 6.1×10^{23} molecules, and a molecule or atom, for they are identical in helium, weighs 6.5×10^{-24} grm.

A great deal of work has been done on radioactive substances with the result that the following facts seem to be established beyond a doubt. First, that the radioactive substances, uranium, thorium and radium are as truly elements for all chemical purposes as any others of our elements. Second, that these elements are continually and spontaneously undergoing transformations into other elements with a decrease in energy which appears in the form of heat and the various rays. One gram of radium gives out 118 grm. calories of heat per hour. Third, that in the case of radium, one of the products of the transformation is a gaseous substance, called radium emanation or niton, and that it is an element of the argon group of inert gases, since it is unattacked by any chemical treatment and has a characteristic spectrum similar to that of the other gases of the group. It has a molecular weight of 224, which is probably also its atomic weight. It is highly radioactive and changes in about a month into other elements, one of which is the undoubted element helium. Fourth, that radium is present in every uranium ore in practically a constant ratio to the uranium content of the ore. Fifth, that a substance having all the properties of lead with the exception of a slightly smaller atomic weight, 206 instead of 207.2, is a final product of the disintegration of uranium. These and other facts of a similar nature are interpreted to mean that radioactive elements decay and pass finally into other and more stable elements, and that they follow the law of successive reactions in going through a number of stages. Radium is one of the decomposition products of uranium, and the radium emanation in turn comes from the radium and goes on into helium, etc.

Some idea of the kind of evidence upon which these conclusions are based may be obtained from the following: Uranium salts which have been kept for some time give out all three kinds of rays. But when such a salt is dissolved in water and ammonium carbonate added until the precipitate which first forms is redissolved, a very small residue is left which gives no alpha rays but has all the beta and gamma activity of the original salt. The uranium carbonate which has redissolved has all the alpha activity of the original compound but gives rise to no beta or gamma rays. The undissolved precipitate is called uranium-X, and is chemically unlike uranium. If the uranium carbonate be reconverted into the nitrate and then reprecipitated and dissolved by ammonium carbonate, no farther precipitate of uranium-X will be formed. But let both the uranium-X and the uranium preparation stand for some time, and it will be found that at the end of about 24 days the uranium-X will have lost half of its activity and the uranium will have regained half of the beta and gamma activity which it lost, and that these changes will go on until finally the uranium will recover its original activity. If now it be reprecipitated and redissolved by ammonium carbonate, a further residue of uranium-X will be obtained. This series of operations may be repeated as often as desired with the same sample of uranium, and it will always be found that when the repetition is made immediately that no further residue of uranium-X can be obtained, but after standing for some time it can always be secured. Therefore, uranium-X is something which grows in a uranium compound and which gives off beta and gamma rays and is half transformed into something else in 24 days, while uranium passes into uranium-X with the production of alpha rays. There is evidence that this uranium-X really consists of two substances uranium-X_1 and uranium-X_2 and that X_1 changes into X_2 and the latter into uranium 2 which passes into a substance called ionium which goes into radium and this into radium emanation and so on as shown in the table on p. 499.

The following table represents the results of an immense amount of labor on the part of many investigators together with something of the theoretical explanation of the phenomena. While it contains a number of points which are still somewhat in question, it is, on the whole, worthy of confidence as a working theory and should be carefully studied. In the first column, is given the group and the sub-family in the periodic system of the element whose name begins the same horizontal line in the second column. The second column gives the equations representing the successive radioactive transformation of the element uranium. The figures just below the names of the elements are the rounded values for their atomic weights. The third column gives the rays produced, omitting the γ rays because these are produced by the β rays. In the last column, the average lives of the atoms of the radioactive elements are given.

oups in riodic ystem	Theoretical Transformation Series				
	Element transformed and atomic weights	Products and atomic weights		Rays	Average life
6 Left	Uranium 1 238	= Uranium X_1 234	+ Helium 4	α	8 × 10^9 years
4 Left	Uranium X_1 234	= Uranium X_2 234	+ Electron 1/1800	β	35.5 days
5 Left	Uranium X_2 234	= Uranium 2 234	+ Electron 1/1800	β	1.65 minutes
6 Left	Uranium 2 234	= Ionium 230	+ Helium 4	α	3 × 10^6 years
4 Left	Ionium 230	= Radium 226	+ Helium 4	α	2 × 10^5 years
2 Left	Radium 226	= Niton 222	+ Helium 4	α	2.44 × 10^3 years
0	Niton 222	= Radium A 218	+ Helium 4	α	5.55 days
6 Right	Radium A 218	= Radium B 214	+ Helium 4	α	4.3 minutes
4 Right	Radium B 214	= Radium C 214	+ Electron 1/1800	β	38.5 minutes
5 Right	Radium C 214	= Radium C′ 214	+ Electron 1/1800	β	28.1 minutes
6 Right	Radium C′ 214	= Radium D 210	+ Helium 4	α	10^{-6} seconds
4 Right	Radium D 210	= Radium E 210	+ Electron 1/1800	β	24 years
5 Right	Radium E 210	= Radium F 210	+ Electron 1/1800	β	7.2 days
6 Right	Radium F 210	= End (lead) 206	+ Helium 4	α	196 days
4 Right	End lead 206				

For example, the table shows that uranium I, atomic weight 238, is a member of the left-hand family of group 6 in the periodic system, and that the theory says that an atom of uranium I spontaneously decomposes into an atom of uranium X_1, atomic weight 234, and an α particle which is, by theory, an atom of helium, atomic weight 4, carrying two charges of positive electricity.

According to this theory, the average life of the atom of uranium is 8×10^9 years; but, just as many men live far beyond the average life of a man, so there will be uranium left in any given sample of the element long after it has been in existence 8×10^9 years.

Uranium X_1 belongs to group 4 two groups lower than uranium 1, and an inspection of the table will show that each transformation which produces α rays gives a product which stands two groups lower in the periodic system with an atomic weight four units smaller than the parent element. A transformation which gives β rays yields a product standing one group higher than its parent, and having practically the same atomic weight because the mass of the β rays is so small that it may be neglected.

There are eight transformations yielding α rays between uranium 1 and the final product. Since each of these lowers the atomic weight four units, the atomic weight of the end product should be $238.2 - 8 \times 4 = 206.2$.

Every uranium ore contains a substance which is precisely like lead in all its chemical and physical properties including the spectrum except that the atomic weight is smaller than that of ordinary lead, 206.4 in the purest ore, instead of 207.2 and its density is also slightly less. Thorium, atomic weight 232.4, undergoes six α-ray transformations and therefore should yield a final product having an atomic weight of $232.4 - 24 = 208.4$. The thorium ores also contain a lead-like substance exactly like ordinary lead except that in this case the atomic weight is 208.4 instead of 207.2. These three kinds of lead differing only in their atomic weights are called isotopes, which may be defined as elements very similar in their chemical and physical properties, differing somewhat in atomic weight, but all occupying the same position in the periodic system. Radium B and radium D are also isotopes of lead. Uranium and uranium 2 are isotopes, and neon is now generally considered to be a mixture of isotopes of atomic weights 20 and 22.

The facts of radioactivity and the theoretical interpretation of them have led to the hypothesis that atoms are complex, consisting of a positively charged nucleus, which constitutes most of the mass of the atom, surrounded by negatively charged electrons, revolving in rings, sufficient in number to balance the itive charge on the nucleus. The hydrogen atom is supposed ɔe the simplest of all and consists of a nucleus carrying one itive charge with one electron revolving around it.

he further hypothesis is now being made that the nucleus of atom of any other element is made up by the combination of lei of hydrogen atoms and electrons, the latter not being sufent in number to balance the positive charge on the hydrogen lei. For example, a helium atom is imagined as made up the combination of four hydrogen nuclei and two electrons ting to form a new nucleus carrying two positive charges und which two electrons carrying two negative charges reve making an electrically neutral atom. In the case of elements having a higher atomic weight than helium the leus is imagined to be made up of as many helium nuclei there are multiples of 4 in the atomic weight plus enough hygen nuclei to complete the atomic weight. That is, the rogen nucleus is supposed to be made up of three helium lei, plus two hydrogen nuclei, plus one electron the whole rogen atom then would have seven electrons revolving around While all these speculations concerning the nature of atoms very interesting, the student will of course recognize that y are very far from being established facts.

he number of electrons revolving around the nucleus of an m is the same as what is called the atomic number of that nent; *i.e.*, the atomic number of hydrogen is 1; of helium, 2; ithium, 3; of nitrogen, 7, and so on. A periodic system can prepared using the atomic numbers of the elements instead of ir atomic weights as the basis of the arrangement. In this e it is noteworthy that no exceptions such as were made with on and potassium, or tellurium and iodine are necessary to ıg the elements into their proper relations. Hence the atomic nbers are apparently more closely related to the properties of elements than are the atomic weights. Isotopes have the ıe atomic number.

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	Symbol	Combining weight		Symbol	Combining weight
Aluminum	Al	27.1	Molybdenum	Mo	96.0
Antimony	Sb	120.2	Neodymium	Nd	144.3
Argon	A	39.88	Neon	Ne	20.2
Arsenic	As	74.96	Nickel	Ni	58.68
Barium	Ba	137.37	Niton (radium emanation)	Nt	222.4
Bismuth	Bi	208.0			
Boron	B	11.0	Nitrogen	N	14.01
Bromine	Br	79.92	Osmium	Os	190.9
Cadmium	Cd	112.40	Oxygen	O	16.00
Calcium	Ca	40.07	Palladium	Pd	106.7
Carbon	C	12.005	Phosphorus	P	31.04
Cerium	Ce	140.25	Platinum	Pt	195.2
Cesium	Cs	132.81	Potassium	K	39.10
Chlorine	Cl	35.46	Praseodymium	Pr	140.9
Chromium	Cr	52.0	Radium	Ra	226.0
Cobalt	Co	58.97	Rhodium	Rh	102.9
Columbium	Cb	93.1	Rubidium	Rb	85.45
Copper	Cu	63.57	Ruthenium	Ru	101.7
Dysprosium	Dy	162.5	Samarium	Sa	150.4
Erbium	Er	167.7	Scandium	Sc	44.1
Europium	Eu	152.0	Selenium	Se	79.2
Fluorine	F	19.0	Silicon	Si	28.3
Gadolinium	Gd	157.3	Silver	Ag	107.88
Gallium	Ga	69.9	Sodium	Na	23.00
Germanium	Ge	72.5	Strontium	Sr	87.63
Glucinum	Gl	9.1	Sulfur	S	32.06
Gold	Au	197.2	Tantalum	Ta	181.5
Helium	He	4.00	Tellurium	Te	127.5
Hydrogen	H	1.008	Terbium	Tb	159.2
Indium	In	114.8	Thallium	Tl	204.0
Iodine	I	126.92	Thorium	Th	232.4
Iridium	Ir	193.1	Thulium	Tm	168.4
Iron	Fe	55.84	Tin	Sn	118.7
Krypton	Kr	82.92	Titanium	Ti	48.1
Lanthanum	La	139.0	Tungsten	W	184.0
Lead	Pb	207.20	Uranium	U	238.2
Lithium	Li	6.94	Vanadium	V	51.0
Lutecium	Lu	175.0	Xenon	Xe	130.2
Magnesium	Mg	24.32	Ytterbium	Yb	173.5
Manganese	Mn	54.93	Yttrium	Yt	88.7
Mercury	Hg	200.6	Zinc	Zn	65.37
			Zirconium	Zr	90.6

[illegible]
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